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Sorption and desorption of chlorinated hydrocarbon pesticides by clay minerals

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Department:

SORPTION AND DESORPTION OF CHLORINATED HYDROCARBON PESTICIDES BY CLAY MINERALS

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ABSTRACT

This thesis describes the sorption and desorption of chlorinated hydrocarbon pesticides by clay minerals under laboratory controlled environmental systems. Particular emphasis was directed toward the investigation of the fundamental adsorption phenomena which occurred in selected pesticide-clay systems. The effects of certain environmental stresses, including pH, temperature and salt (NaCl) concentration of water, on the behavior of sorption and desorption were also studied.

Pesticides selected for this study included DDT, dieldrin and heptachlor, and clay minerals employed were kaolinite, montmorillonite and illite. The adsorption rate and equilibrium were evaluated by batch techniques employing completely mixed systems while the effects of the environmental factors on the sorption and desorption were investigated with laboratory controlled aquatic models.

Results obtained from this study disclosed that the chlorinated hydrocarbon pesticides were rapidly adsorbed by the experimental clay minerals; in most cases the adsorption equilibria were reached within two hours of reaction. After the pesticides had been adsorbed on the clays, desorption of the pesticides occurred only to a very small extent. It is believed that the uptake of the organochlorine insecticides by the clay minerals is a process of chemical adsorption which involves the formation of certain types of high strength bonding.

The pH, temperature and salt (NaCl) concentration of water did not appear to exert significant effects on the sorption and desorption of the chlorinated hydrocarbon pesticides by the clay minerals.

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CHAPTER I

INTRODUCTION

Since the publication of Silent Spring by Carson (12) in 1962 there has been a rapidly growing public concern about the widespread contamination of pesticide residues in the environment. This is not only because pesticides are highly toxic, but also because they have been used in ever increasing quantity and variety since the last fifteen years. It was reported in 1965 (35) that the daily application of pesticides to crops and soil averaged approximately two million pounds, and that a tenfold increase in pesticide consumption could be expected within the next 15 years. Organic pesticides comprise a wide spectrum of chemical substances including insecticides, herbicides, fungicides, rodenticides, miticides and nematocides ; among these, the consumption of chlorinated hydrocarbon insecticides totaled one-fourth of all pesticides used in 1965 (45).

Most pesticides are applied to vegetation or soil in order to control agricultural pests or weeds. After application the fate of these pesticides seems to be very complex and unpredictable, at least as far as our present knowledge is able to determine. Some of the pesticides could be lost by direct volatilization, natural microbial degradation (41) or chemical oxidation (43). Other pesticides could be leached through soil by rainfall or irrigation water, thereby contaminating the ground water (67); certain groups of pesticides could be adsorbed on particular matter such as soils and finely divided clays, which might be carried by storm runoff into the natural waters. From the viewpoint of water pollution control, the latter two cases are of particular concern since they both pose an alarming threat for degrading the quality of natural water resources.

Widespread contaminations of chlorinated hydrocarbon insecticides in

the environment have caused great public concern today. This is primarily because these materials are used to a very large extent, extremely toxic, and highly persistent due to their resistance to biodegradation (34,54). Also, chlorinated hydrocarbon pesticides are so extremely hydrophobic in nature that they may be easily adsorbed on soils and finely divided clays following their applications. Some of these "pesticide-coated" soils and clays may be transported with storm runoff to natural aquatic bodies. Under certain conditions part of the sorbed pesticides could be desorbed and released into the water phase in order to maintain an equilibrium system; as a consequence, the desorption of pesticides provides a continuous supply of these materials to water and constitutes a serious water pollution problem. In fact, residues of chlorinated hydrocarbon pesticides have been detected in almost all major U.S. rivers (9,56,57), with larger concentrations being found in the sediment phase than in the overlying water (5).

In estimating the transport of pesticides in rivers and streams, or the buildup of pesticides in lakes, reservoirs and other aquatic bodies, or in estimating the potential contamination of ground waters by leaching pesticides, it is important to understand fully the sorption and desorption of these pesticides in soils and aquatic sediments, of which clay is a major component.

Up to now there has been only a limited number of investigations conducted to evaluate the sorption and desorption of organic pesticides by soils or aquatic sediments. Most of these investigations were confined to the survey type of the field work. Undoubtedly, there are many factors governing the complex mechanism of pesticide sorption and desorption; among these, of particular importance may be the nature of pesticides, soil or sediment constituents, organic materials present in both the sediment and the liquid phase, and several other environmental factors

such as pH, temperature, and salt concentration of water. All of these parameters must be fully investigated before the fate of pesticides can be predicted with reasonable certainty.

A. Objectives

The purpose of this investigation was to investigate the fundamental sorption and desorption reactions of selected chlorinated hydrocarbon pesticides with clay minerals under laboratory controlled environmental conditions. Particular emphasis was directed toward the evaluation of the rate of uptake and the adsorption isotherm in each selected pesticide-clay combination and the effect of several important environmental factors such as pH, temperature and salt (NaCl) concentration of water on the pesticides sorption and desorption reactions.

B. Scope

Three types of chlorinated hydrocarbon pesticides were chosen for this study; these included DDT, dieldrin and heptachlor. These three chemicals are among the most common types of chlorinated hydrocarbon pesticides used in the United States.

Kaolinite, illite and montmorillonite were the three types of clay minerals selected in this study. All of these three clay minerals are of crystalline form and most commonly found in soils and aquatic sediments.

The experimental study was conducted in two steps. The first step used the batch technique to evaluate the rate of uptake and the equilibrium of adsorption for the three selected pesticides with the three different types of clay minerals. The second step employed a series of aquatic model systems to ascertain the effect of several important environmental factors, including pH, temperature and salt (NaCl) concentration of liquid

solution, on the pesticide sorption and desorption reactions. Only one pesticide-clay combination was employed in the aquatic model studies.

Before the performance of the above two major experimental studies, a series of supplemental tests were conducted to evaluate the physical and chemical characteristics of the test materials so that certain suitable experimental controls could be duly provided in the subsequent adsorption studies.

CHAPTER II

LITERATURE REVIEW

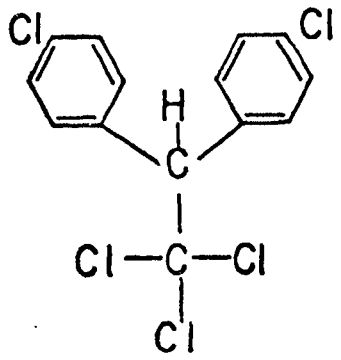
A survey of literature was made on the subjects pertinent to this study. The collected information is grouped into the following six areas, all of which are presented in the following subsequent paragraphs: (A) structures and properties of the chlorinated hydrocarbon pesticides selected for this study, (B) nature of the clay minerals selected for this study, (C) sorption and desorption of organic pesticides by clay minerals, (D) reactions of clay minerals with organic materials, (E) contamination of pesticides in the environment, and (F) toxicity of pesticides to aquatic organisms.

A. Structures and Properties of the Chlorinated Hydrocarbon Pesticides Selected for This Study

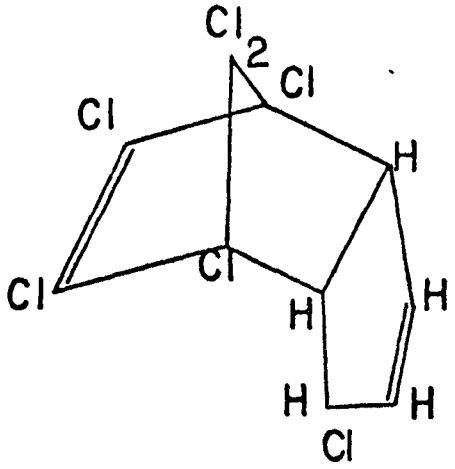
DDT, dieldrin and heptachlor are the three chlorinated hydrocarbon pesticides selected for this study. Each of these three pesticides represents a distinct chemical structure of those chlorinated hydrocarbon pesticides most commonly found in agricultural applications. The chemical structure, physical and chemical properties of each of these three pesticides are discussed as follows:

1. DDT: The old name for the insecticide DDT is dichlorodiphenyl trichloroethane; now the commonly accepted name is 1,1,1-trichloro-2, 2-bis-(p-chlorophenyl)-ethane. It has a chemical formula of $(p\text{-}ClC_6H_4)_2\text{-}CHCCl_3$. The structural formula for this compound is shown in Fig. 2-1.

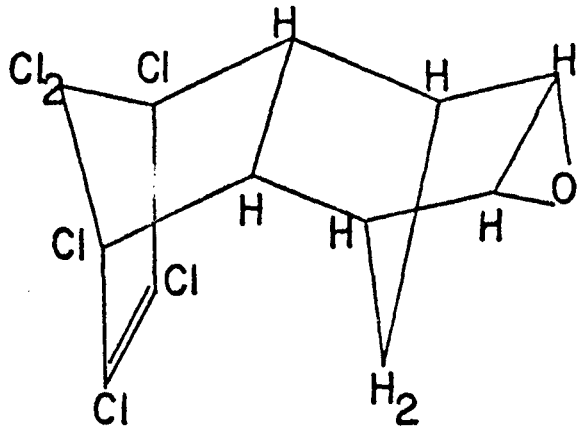
Although most handbooks of chemistry list DDT as insoluble in water,



DDT



HEPTACHLOR



DIELDRIN

Fig. 2-1. Structures of Pesticides Studied

this chemical actually has a sparse solubility on the order of part per billion (ppb). Robeck et al. (47) reported that the apparent solubility of organic pesticides is partially a function of the size of pesticide permitted to remain in the liquid sample in the solubility determination; for DDT, the aqueous solubilities were found to be 16 and 40 ppb, respectively, when the maximum particle sizes allowed in water were 0.05 and 5 microns.

DDT is quite stable to the action of heat; it does not decompose at temperatures below 195°C, but most DDT of technical grade will decompose at about 100°C due to the presence of some impurities such as iron, aluminum, and chromium. Most solvents tend to inhibit this DDT decomposition; however, the decomposition is accelerated by chloro- and nitro-benzenes (43).

In the alcoholic alkaline medium such as KOH solution, DDT is dehydrochlorinated to form 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethylene (DDE). Trace amounts of iron, aluminum, and chromium salts can act as catalysts for this dehydrochlorination reaction of DDT (24). Under the catalytic action of zinc, DDT can also react with hydrochloric acid and becomes 1, 1-dichloro-2,2-bis-(p-chlorophenyl)-ethane (DDD) (43). Some microorganisms such as Aerobacter aerogenes and actinomycetes (13,46) can also convert DDT into DDD.

Residues of DDT under field conditions are subject to ultraviolet irradiation and are slowly decomposed into noninsecticidal compounds such as 4, 4-dichlorobenzophenone and 2,3-dichloro-1,1,4,4-tetrakis-(p-chlorophenyl)-2-butene (23);the greatest rate of decomposition was found at the wavelengths of 220 mμ to 240 mμ.

2. Dieldrin: Dieldrin is an epoxide of aldrin. At the present time, the accepted chemical name for dieldrin is 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,

4, 4a, 5,6,7,8,8a-octahydro-1,4-endo-exo-5,8-dimethanonaphthalene. Its chemical formula is $C_{12}H_8Cl_6O$. The structural formula for this compound is shown in Fig. 2-1.

Dieldrin is also described as insoluble in water in most chemistry handbooks; actually, the apparent solubility of dieldrin in water ranges from 100 ppb at about 10°C to 300 ppb at 40°C (20). Dieldrin is completely stable to the action of alkali; but when dieldrin is refluxed with halogen acids, the compound of halohydrin of dieldrin is formed. Therefore, hydrogen bromide is an important reagent for analyzing the composition of dieldrin because when dieldrin is treated with anhydrous hydrogen bromide for two hours at room temperature,the bromohydrin of dieldrin is formed (31).

Dieldrin can be converted to aldrin by treatment with acetic and hydrobromic acids(43). Microorganisms (34,41) and ozone (47) can degradate dieldrin to other compounds.

Photodecomposition of dieldrin was observed at 250 mμ to 300 mμ under the laboratory controlled condition (33); the ultraviolet irradiation of dieldrin was found to yield a major product of pentachloro derivative that is less toxic than dieldrin to flies, but more toxic to mice.

3. Heptachlor: The chemical name for heptachlor is 1,4,5,7,8,8-heptachloro-3a, 4,7,7a-tetrahydro-4,7-methanoindene. Its chemical formula is $C_{10}H_5Cl_7$. The structural formula of heptachlor is shown in Fig. 2-1.

Heptachlor is an unsaturated cyclodiene; it is stable under exposure to heat at 160°C, or to light, moisture, and air; it is also stable under prolonged contacts with acids, bases, and oxidizing agents; but it can be slightly degradated under anaerobic biological conditions (34).

B. Nature of the Clay Minerals Selected for this Study

Kaolinite, illite, and montmorillonite are the three types of clay minerals selected for this study. All of these clay minerals are of crystalline form and commonly found in soils and aquatic sediments. The nature of these clay minerals will be presented below according to their mineral structures, crystal shapes, ion exchange capacities and specific surface areas, most of which have been well described by Grim (28,29).

1. Mineral Structures: All clay minerals are layer-lattice alumino silicates; the layers are made up of tetrahedral sheets of silicon oxide and octahedral sheets of aluminum oxide and/or hydroxide, as shown in Figs. 2-2 & 2-3. The terms "tetrahedral" and "octahedral" indicate that the sheets are made up of four-sided (Fig. 2-2a) and eight-sided (Fig. 2-3a) molecular building blocks, respectively. The tetrahedral sheet (Fig. 2-2b) is composed of individual tetrahedra in which the cation silicon is surrounded by four oxygen anions; the octahedral sheet (Fig. 2-3b) is composed of individual octahedra where aluminum is surrounded by six oxygen and/or hydroxyl anions.

Kaolinite consists of a single silica tetrahedral sheet and a single alumina octahedral sheet; the two are tied together into a common sheet by shared oxygen to form the kaolinite unit layer, Fig. 2-4. The unit layers are stacked one above the other and this constant periodicity makes up a kaolinite clay crystal.

Montmorillonite is composed of unit layers consisting of two silica tetrahedral sheets with a central alumina octahedral sheet, as shown in Fig. 2-5. The bonds between the unit layers are weak, and water and other polar molecules can penetrate into these interlamellar spaces and cause expansion; thus, montmorillonite is an "expansible" or "swelling" type of

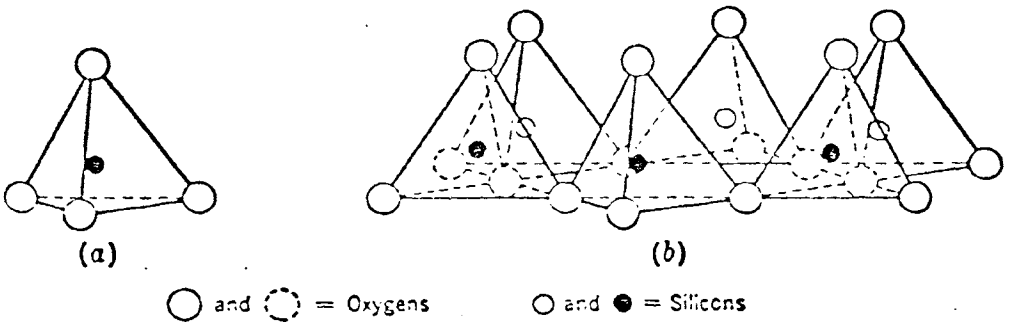


Fig. 2-2. Sheet Structure of the Silica Tetrahedrons

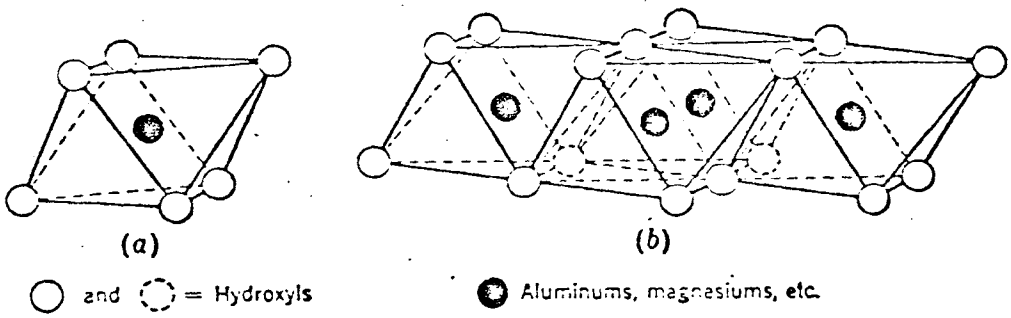


Fig. 2-3. Sheet Structure of the Alumina Octahedrons

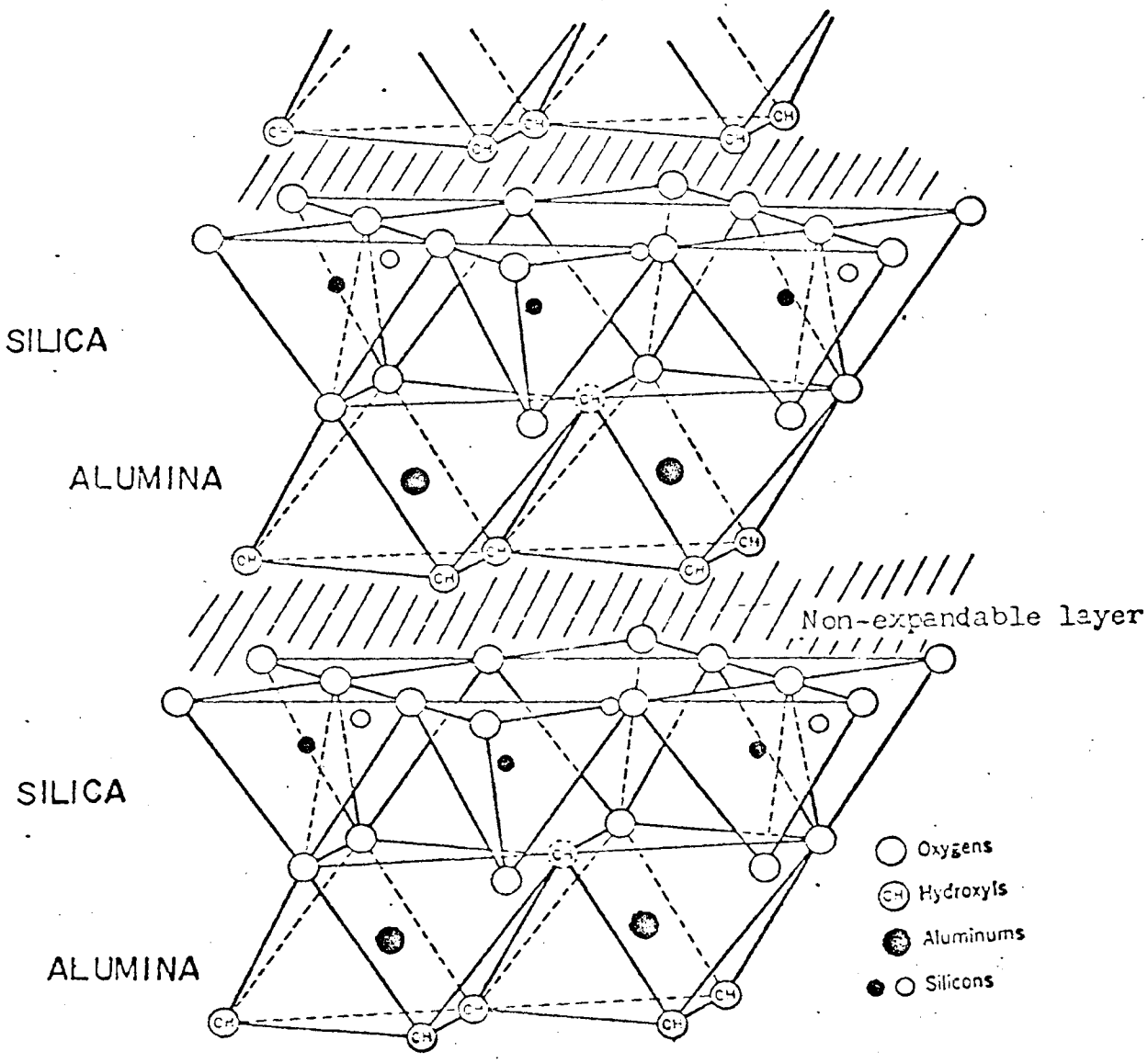


Fig. 2-4. Structural Sketch of Kaolinite

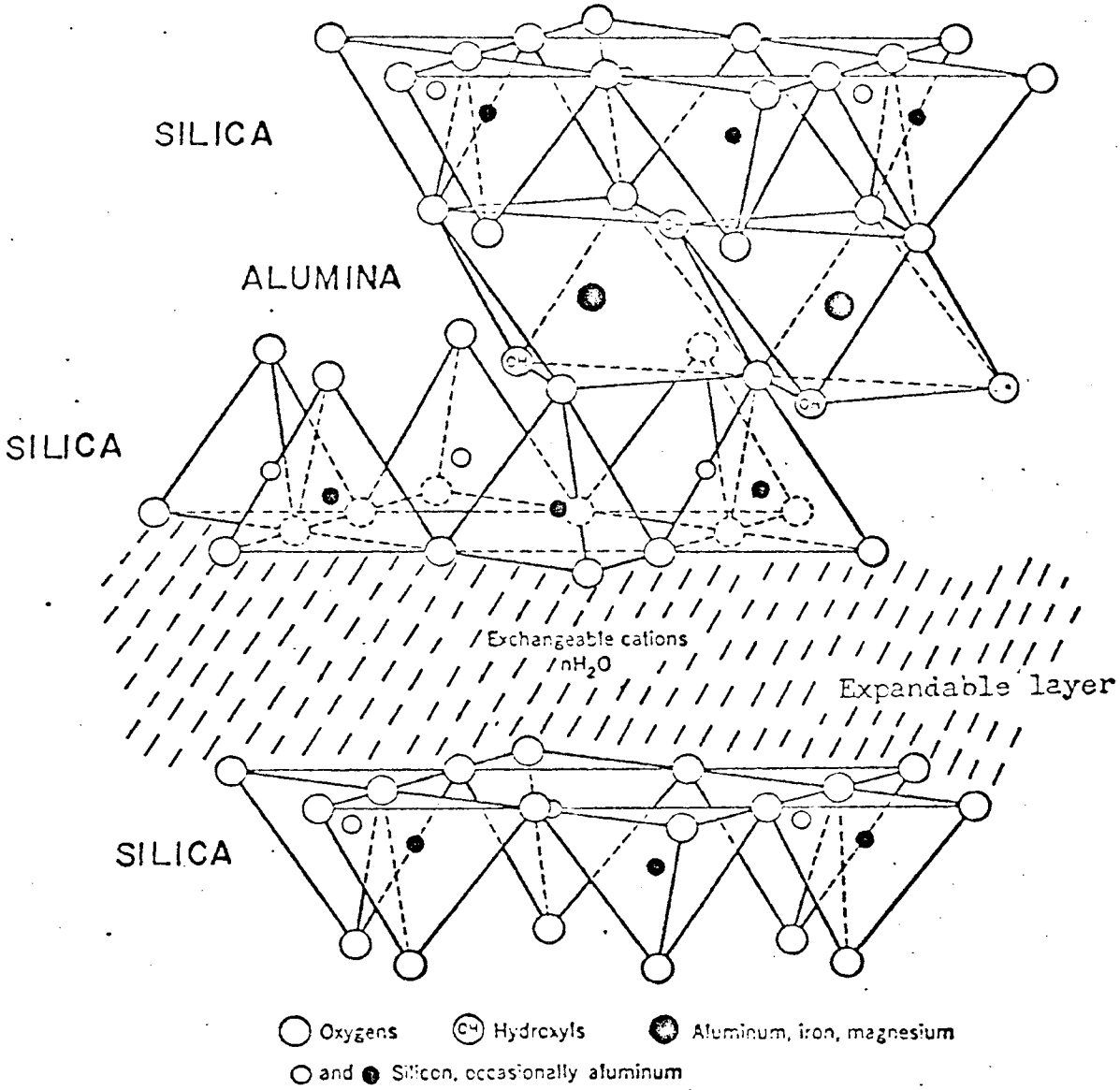


Fig. 2-5. Structural Sketch of Montmorillonite

clay. The charge deficiency due to the isomorphic substitution (i,e., Al^{+3} for Si^{+4} in the tetrahedral layer) in the montmorillonite clay mineral is balanced on the outside of the crystals by such inorganic cations as sodium, calcium, magnesium, and other cations.

Illite has a basic structural unit layer composed of two silica tetrahedral sheets and a central alumina octahedral sheet, Fig. 2-6. This unit layer is similar to that of montmorillonite except that the charge deficiency is balanced by potassium ions which act as a bridge between the unit layers and bind them together, thereby preventing "expansion" or "swelling".

2. Crystal Shapes: Clay minerals are quite variable in their shapes. The crystal shapes of clay minerals are affected by the particular environment in which the clays are formed. The crystal shape of kaolinite may range from a well-crystallized hexagonal grain to ragged and irregular poor-crystalline outline. Illite and montmorillonite contain poorer crystalline fabrics than kaolinite.

Well-crystallized kaolinite has well-formed six-sided flakes, frequently with a prominent elongation in one direction. In poorly crystallized kaolinite, the particles have less distinct six-sided flakes.

The individual particles of montmorillonite are not easy to reveal; in general, the extremely small particles of montmorillonite are grouped to form irregular fluffy masses. In some cases the larger masses appear to be stackings of flake-shaped units without regular outlines.

Illite has small, poorly defined flakes which are commonly grouped together in irregular aggregates. Some of the flakes have a distinct hexagonal outline which causes the particles of illite to have a better-defined edge.

3. Ion Exchange Capacities and Specific Surface Areas: Both the ion

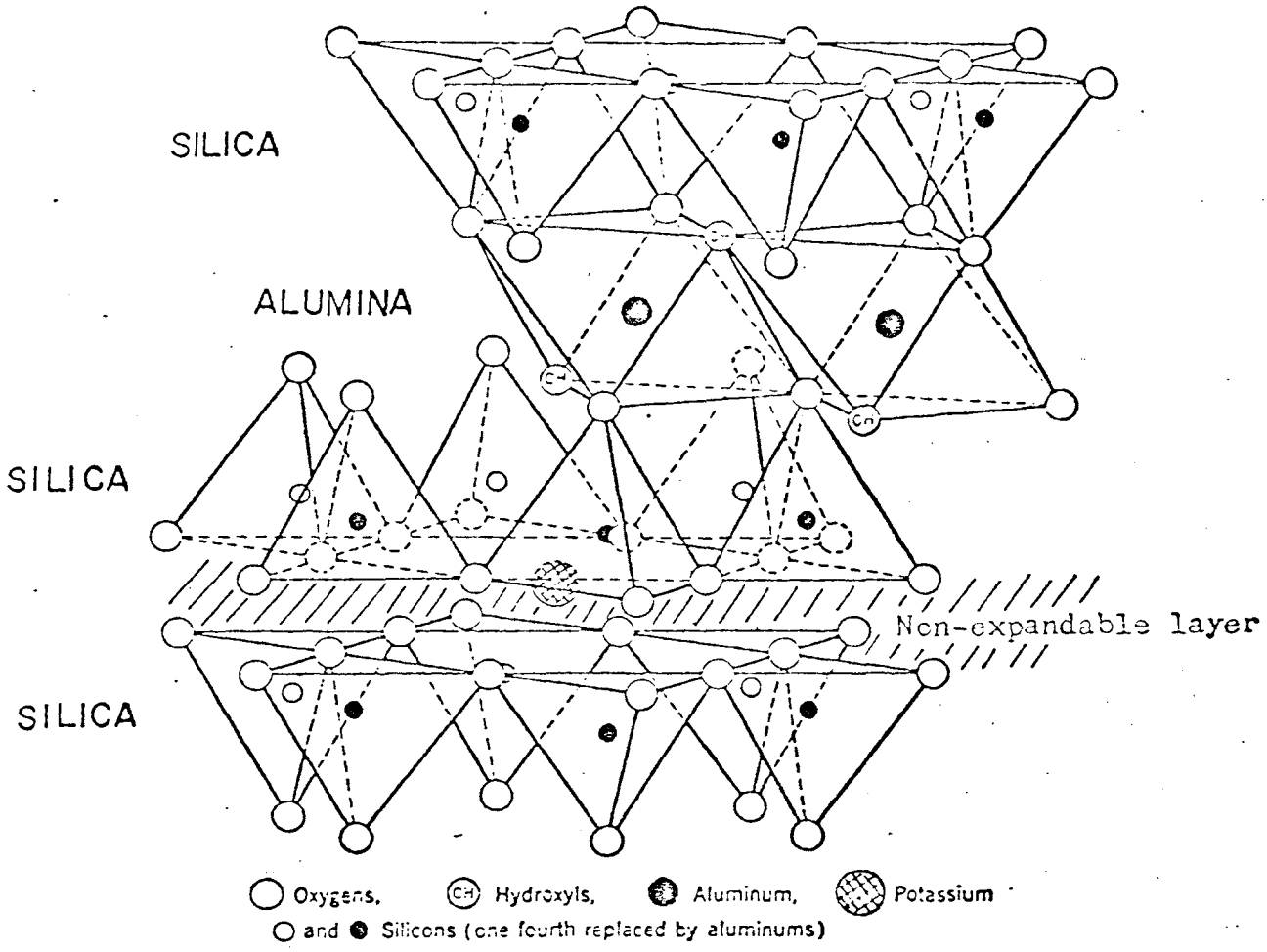


Fig. 2-6. Structural Sketch of Illite

exchange capacity and the specific surface area of a clay mineral are important in affecting the adsorption reaction. The ion exchange capacity of a clay determines its extent of uptake of certain ions. The surface area of a clay provides the necessary sites for adsorbing organic molecules such as pesticides.

The ion exchange capacities (29) and the specific surface areas (62) for kaolinite, illite, and montmorillonite clays are listed as follows:

Table 2-1.

Ion Exchange Capacities and Specific Surface Areas for Several Clays

Type of Clay	Ion Exchange Capacities* (meq/100g)		Specific Surface Area** (m^2/g)
	Cation	Anion	
Kaolinite	3-5	6.6-20.2	11-20
Illite	10-40	-	78-100
Montmorillonite	80-150	23-31	102-109

* After Grim, Reference (29).

** After Wayman, Reference (62).

C. Sorption and Desorption of Organic Pesticides by Clay Minerals

Although in recent years there have been many investigations concerned with the behavior of insecticides in various types of soil, most of these studies emphasized on the evaluation of the interactions between pesticides and soils, and the resulting effects on the residual pesticidal activities. Only relatively few investigators have undertaken the research studies of the pesticide sorption and desorption reactions from the standpoint of

water quality management and pollution control.

Eye (20) studied the adsorption of dieldrin on several types of soil and found that the adsorption at equilibrium followed the Langmuir isotherm. In both equilibrium and column percolation experiments, the cation- and the base-exchange capacities, the specific surface areas, and the clay content of the various soils did not appear to affect the adsorption capacity strongly, but higher organic contents present in soils tended to increase the adsorption capacity.

Chesters (14) conducted an investigation on the adsorption of insecticides on lake sediments in an attempt to evaluate the insecticide accumulation in lakes. The extent of the lindane adsorption was found to be affected by the concentration of suspended sediment, the organic content and the clay content of the sediment, and the amount of lindane already adsorbed on the sediment. The adsorption of lindane was decreased by the presence of iron oxides in the sediment, probably because oxide coating on clay particles may interfere with the surface OH bonding of the clay minerals. The adsorption of lindane in separate sediment fractions was observed to decrease with the increasing particle size of the sediment. Chesters also found that the malathion adsorption was largely controlled by the organic content of the sediment. In the separate sediment fractions, malathion adsorption was also found to decrease with the increasing particle size and the iron oxide content of the sediment sample.

Bowman, Schechter, and Carter (6) studied the behavior of 11 chlorinated hydrocarbon insecticides in eight types of soil under laboratory controlled conditions in order to provide a better understanding and prediction of the fate of these pesticides in the field. Bailey and White (2) reviewed several factors, including pH, temperature, types, nature, and

moisture content of soil, which influenced the sorption and desorption of organic pesticides by soil. Lichtenstein and his colleagues (40) monitored the precipitation of aldrin to the bottom of lake after an aldrin application to water at 10 ppm and found that the presence of lake bottom mud in water enchanced the aldrin precipitation.

Hill and McCarty (34) found that the adsorptions of chlorinated hydrocarbon pesticides on bentonite clay and algae were inversely proportional to the pesticide solubilities; these organochlorine pesticides were more strongly adsorbed on algae than on bentonite clay. Faust and Aly (22) attempted to use kaolinite, bentonite and illite to adsorb organic pesticides from water prior to the chemical coagulation; however, they found that this method was very impractical because data indicated that very little pesticides could be adsorbed on suspended soils and bottom muds in the aqueous system.

D. Reactions of Clay Minerals with Organic Materials

A review of the interactions between clay minerals and organic materials may help in the understanding of the reactions between pesticides and clay minerals. Many studies have shown that organic molecules can react with clays, particularly with montmorillonite (18,19,25,26). In addition, it has been shown that organic compounds with polar active groups can be adsorbed easily by the clay minerals (7,17). The following paragraphs will summarize briefly the reaction of organic materials with montmorillonite, kaolinite and illite clay minerals.

1. Reactions with Montmorillonite: Up to now the reaction of organic matter with montmorillonite has been studied more thoroughly than with any other clay mineral (28). In the reactions with ionic molecules, the organic ions such as gelatin and protein are held around the edges of the montmoril-

lonite clay thereby reducing the water adsorbing capacity of montmorillonite clay (28).

In the adsorption of organic compounds by montmorillonite, the earlier literature (17) postulated that the positive ends of polar organic molecules could be attracted by the negative centers of the montmorillonite clay mineral structure; however, Bradley (7) concluded that the polar organic molecules were held to the clay surface through the hydrogen bonding such as C-H...O bond.

Recently, Russell et al. (49) studied the adsorption of 3-aminotriazole by montmorillonite; they found that the 3-aminotriazole molecule was protonated when it was adsorbed on the montmorillonite clay surface to form the 3-aminotriazolium cation. Russell and his colleagues believed that the protonation of the 3-aminotriazolium was the result of the direct coordination of the highly polarized water molecules with polyvalent cations such as Ca^{+2}, Cu^{+2}, Ni^{+2}, Al^{+3}.

2. Reactions with Kaolinite and Illite: Grim et al. (30) have shown that the water sorption properties of kaolinite and illite were reduced by the ionic reactions of these clay minerals with organic ions; they found that the quantities of organic cation adsorbed on kaolinite and illite were small, with the adsorption being a little greater on illite than on kaolinite.

Bradley (7) pointed out that the adsorption of polar molecules would take place on the surfaces of kaolinite and illite. He also indicated that organic molecules could not penetrate into the spacings between the unit layers of kaolinite or illite since these two clay minerals are non-expansible.

E. Contamination of Pesticides in the Environment

Pesticides are applied to farm lands, forests, lakes, and urban areas in order to control pests. Some pesticides could be lost by direct volatilization, natural microbial degradation or chemical oxidation. Through volatilities and aqueous solubilities, many pesticides have been detected in air, surface waters and ground waters. Pesticides have also been found in birds, fish forest animals and human bodies.

Hindin et al. (36) have reported that some pesticides are detected in air; these pesticides were volatilized to atmosphere after application and could be transported in air by wind and deposited on areas remote from the original application. Weibel et al. (64) identified traces of pesticides present in the precipitation at Cincinnati in 1965; they found that the precipitation contained a high concentration of DDT, DDE, chlordane, heptachlor epoxide, dieldrin etc., and these pesticides were transported by air over a long distance. Similarly, Cohen and Pinkerton (15) also identified some pesticides in rain water.

The presence of pesticides in surface waters may be due to the direct application of these chemicals on waters, the agricultural runoff containing pesticide residues, the clean-up of equipment used in the pesticide application, or the industrial discharge of pesticide wastewater. Some pesticides can reach ground waters by percolation through the soil formation or transportation through the direct channelings between surface and ground waters. In some area, the pesticide contamination in the well water supply (50,60) was found to persist for almost five years. Middleton and Lichtenberg (44) found that a concentration of one to 20 ppb of DDT was present in several rivers, and that an estimated concentration of one ppb of aldrin was present in the Snake River; Breidenbach and Lichtenberg (9) reported that an approximate concentration of one to two ppb of DDT and

dieldrin was found in 10 streams in the United States in 1962; Breidenbach et al. (8) made a synoptic chlorinated hydrocarbon pesticides survey in some major U.S. rivers during 1957-65. These surveys revealed that all the major U.S. rivers had been contaminated by pesticides.

The study of Clear Lake, California (37) disclosed that the lake had been contaminated with pesticides, which also exerted a significant effect on higher food chain organisms. Pesticides had also been found in birds and mammals; a pesticide concentration as high as 1600 ppm was detected in the flesh of dying grebes at Clear Lake, California. Bailey and Hannum (3) also reported that pesticides were distributed throughout every segment of the aquatic environment in California. Another investigations by Welch and Spindler (65) also showed that fishes, including marine species, had accumulated pesticides in their bodies.

In addition, the accumulation of pesticides residues in human body tissues had been investigated (51); the findings indicated that pesticides could be accumulated in human body to a very high concentration; for example, two to 31 ppm of DDT had been identified in fat tissues of human bodies. Generally speaking, pesticides have been found to spread throughout the environment and they represent one of the major groups of contaminants which have caused serious environmental pollution problems.

F. Toxicity of Pesticides to Aquatic Organisms

Pesticides are designed to eradicate pests and they are also potentially dangerous to aquatic organisms, animals and human. Many tests have been conducted to determine the toxicity of pesticides to aquatic life and the effects of pesticides on the environment. Field studies have been made by a designed spraying program in order to determine the extent of toxicity of pesticides to aquatic organisms. Laboratory bioassays were

also made on fish, insects and mammals in order to evaluate the relative toxicity of these materials to different types of organisms.

The evaluation of the toxicity of pesticides was undertaken when DDT was first introduced in 1940's. The earlier studies (52,55) demonstrated that the pesticide formulation and the method of application influenced the toxic effects of DDT to aquatic life. The routine hand applications of DDT at 0.1-0.05 lb/acre was found to result in a reduction of fish food organisms (55). Many kills of aquatic organisms have also occurred following the forest spraying and treatment of land area with pesticides. Many investigators (11,27,38) reported that a large amount of aquatic life including marine organisms had been reduced after application of pesticides; in many cases the toxic effects of pesticides persist for a period of several years.

Laboratory bioassay studies have been carried out for several years in many USPHS laboratories (56). The results of these studies indicated that the chlorinated hydrocarbons are more toxic to aquatic organisms than the organic phosphours compounds (56), and endrin was found to be the most toxic pesticide to fish at the present time. Endrin was also found to be the major toxic material which killed many fish in the Lower Mississippi River in the winter periods from 1960 to 1964 (59).

In general, organic pesticides are now used in such a large quantity that they have been recognized as one of the major environmental pollutants today. Fish kills due to pesticides rank next to kills due to all industrial wastes taken as a group (56). In addition, trace amounts of pesticide are subjected to biological concentration and can pass through the food chain and accumulate in high levels within human bodies. Therfore, sanitary engineers must face and solve the pesticide pollution problem in order to protect the public health.

CHAPTER III

MATERIALS AND EQUIPMENT

The materials and equipment employed in this research study are described in this chapter. A brief justification for the selection of some experimental materials such as pesticides and clay minerals will also be discussed.

A. Materials

The major items of the experimental materials which are of pertinent significance to the analysis and explanation of the experimental data include pesticides, clay minerals, carrier solvent for dispersing pesticides in water, and the pesticide extraction solvent.

1. Pesticides: The pesticides selected for this investigation were DDT, dieldrin, and heptachlor, all of which are chlorinated hydrocarbons and commonly found in agricultural applications. DDT represents a chlorinated diphenyl compound; dieldrin is an epoxidized cyclodiene; and heptachlor is an unsaturated cyclodiene. Consumption of the pesticides consisting of the above three general chemical structures represents more than 60 per cent of all chlorinated hydrocarbons used in the United States (34). In addition, during 1965 the consumption of chlorinated hydrocarbons totaled approximately one-fourth of all the pesticides used in the United States (45).

Chlorinated hydrocarbon pesticides in natural water are of particular concern because they are extremely persistent in the environment and highly toxic to fish and many other aquatic organisms; they can also exert adverse effects on man through his drinking water supplies and food. It must be

pointed out that trace amounts of pesticides can be physiologically concentrated in animal tissues to levels sufficient to kill the animal.

A technical grade DDT supplied by Agricultural Chemical Division of Geigy Chemical Corporation, Ardsley, New York, was used in this study. A gas chromatographic analysis of this DDT sample revealed that it contained 76 per cent p,p'-isomer, 23 per cent o,p'-isomer and less than one per cent of other related compounds.

A technical grade dieldrin used in this study was supplied by Shell Chemical Company, New York, New York, while a 99.8 per cent analytical reference grade heptachlor was obtained from Velsicol Chemical Corporation, Chicago, Illinois. The aqueous solubilities of these three pesticides were determined in the laboratory; the detail procedure and results are described in Chapter IV (p. 43).

2. Clay Minerals: Three types of clay minerals were selected for this study; these were kaolinite, illite and montmorillonite, all of which are of crystalline form and commonly found in soils and aquatic sediment. Each of these clays also represents a distinct chemical structure and nature as described previously in Chapter II.

All of the three types of clay minerals used in this investigation were supplied by the General Research Laboratory of W. S. Dickey Clay Manufacturing Company, Pittsburg, Kansas. Because the specific surface area of a clay particle may exert a significant effect on adsorption reactions, all clay samples used in this study were properly prepared before experiments. After bags of clays were obtained from the supplier, they were properly ground and sieved. The fractions of clays passing through the U.S. Standard Sieve No. 200 (A.S.T.M. Specifications) were used for the experiments. The opening of this sieve is 74 microns, or 0.0029 inches.

A microscopic examination employing a Whipple Disc was made to determine the size of clay particles. The approximate particle size of each clay sample was found as follow:

kaolinite	1 micron
montmorillonite	1-2 microns
illite	1-2 microns

In addition to the determination of the clay particle size, the organic content of these clay samples and the pH of the clay-water suspensions were also evaluated; the detail procedure and results are discussed in Chapter IV (p. 55).

3. Carrier Solvent for Dispersing Pesticides in Water: For the following two reasons a carrier solvent was used to disperse the pesticides in water:

(a) All of the three chlorinated hydrocarbons used in this study are relatively insoluble in water. It is difficult or even impossible to dissolve completely a fixed quantity of pesticide in water.

(b) It was found by the gas chromatographic analysis in the laboratory that the three pesticide samples employed in this work contained some impurities which had much higher solubilities than the pesticide chemicals. Therefore, after dispersing an excessive amount of pesticides directly in water, the quantity of impurities dissolved in water would outnumber the amount of pesticide dissolved. This resulted in a number of impurity peaks observed in the gas chromatographic analysis of the pesticide concentration for the sample.

As a consequence, an ACS grade acetone was used as the carrier solvent for the preparation of standard pesticide stock solutions since acetone is a good solvent for chlorinated hydrocarbon pesticides and also readily miscible with water. In addition, in a preliminary adsorption study, which

is presented in Chapter IV (p. 58), it was found that the adsorption of dieldrin on montmorillonite was not influenced materially by the use of acetone as the carrier solvent.

A standard pesticide-acetone stock solution of 100 mg/l was prepared for each kind of pesticide. The stock solutions were kept in refrigerator. The aqueous pesticide solutions used in the experiments were prepared from diluting these standard solutions with the calculated amount of distilled water.

4. Extraction Solvent: There are several kinds of solvent or mixture of solvents which have been used by many investigators for the liquid-liquid extraction of pesticides from aqueous solutions; for example, a mixture of 2:1 of benzene:isopropanol (66), or 1:1 of ethyl ether:petroleum ether (58), or chloroform (58) has been used. Most of the research workers (10,34,39,61) have used or recommended hexane as the extraction solvent because hexane is a good solvent for chlorinated hydrocarbon pesticides and particularly suitable for the subsequent gas chromatographic analysis of the pesticide extract. Therefore, an ACS grade hexane was used as the extraction solvent in this study.

B. Equipment

The major items of equipment used in this research study were gas chromatograph, magnetic stirrers, centrifuge, high-speed mixer and pH meter, all of which are described briefly as follows :

1. Gas Chromatograph: A Varian Aerograph Gas Chromatograph, Model 1520-1B, was employed for the analysis of pesticide concentrations in aqueous solutions. This instrument is a product of Varian Aerograph, Walnut

Creek, California, and is shown in Fig. 3-1.

This gas chromatograph has a dual-channel system. Each channel has its own flow controller, sample-injector tube, column and detector. Therefore, each single channel can be operated as an independent system.

The electron capture detector* was employed for the quantitative measurement of trace amounts of pesticides present in samples. This type of detector is tremendously sensitive to chlorinated compounds and therefore, able to analyze a pesticide concentration in the ppb range (32). It is conveniently not sensitive to ordinary volatile organic compounds which are invariably present in extracts of plant material. Thus, troublesome and messy clean-up procedures are largely avoided.

It has been reported (32) that some chlorinated hydrocarbon pesticides can be easily decomposed upon their contact with any hot metal; therefore, a Pyrex glass injector tube* was inserted into the metal sample injector. Also, a Pyrex glass column* packed with 5% Dow-11 on 80/100 mesh High performance Chromosorb W* was employed. The following operation conditions were used for the gas chromatographic analysis of the experimental pesticides:

column	temperature	180°C
detector	temperature	200°C
injector	temperature	200°C
carrier	gas	N_2 at 40 ml/min.

The signal output from the gas chromatograph was recorded on the Speedmax W Recorder, a product of the Leeds and Northrup Company, Philadelphia, Pennsylvania.

The detail procedure for the gas chromatographic analysis of the chlorinated hydrocarbon pesticides is described in the Appendix I.

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* Products of Varian Aerograph, Walnut Creek, California.

Fig. 3-1. Varian Aerograph Model 1520-1B Gas Chromatograph

2. Magnetic Stirrer: Five Fisher Jumbo-Size Magnetic Stirrers, Fig. 3-2, were used in this study to provide agitation for the test clay suspensions. These stirrers are designed for use with large volumes of liquid or with liquids of high viscosity. A Teflon-coated stirring bar of 2-7/8 inches in length was used to agitate the test clay suspensions. The motor is capable of speeding up to 1550 rpm for solutions having a low viscosity.

3. Centrifuge: An International Clinical Centrifuge, Model CL as shown in Fig. 3-3, was used to separate clay materials from aqueous pesticide solutions. This instrument is a product of the International Equipment Company, Needham Heights, Massachusetts.

The centrifuge is equipped with a four-place centrifuge head which can take four 50 ml capacity centrifuge tubes. The maximum attainable speed is 3200 rpm providing an average centrifugal force of 1610 g.

4. High Speed Mixer: A VirTis aero-seal chemixer, Fig. 3-4, was used to disperse pesticides in water. This instrument is a product of The VirTis Company, Inc., Gardiner, New York. The mixer has a special razor sharp stainless steel blades or impellers operating at speeds from 100 to as high as 17,000 rpm by a 1/5 HP motor. The assembly includes Pyrex glass container with deep flutes, stainless steel shaft and blades, inert Teflon cap, motor and rheostat. The aerosol-free assembly eliminates harmful aerosols often encountered in homogenizing, blending and emulsifying techniques. A liquid volume varying from 100 ml to 4,000 ml may be processed at one time by simply using containers of appropriate-size.

5. pH Meter: The pH measurements were made with a Beckman Zeromatic pH meter, Fig. 3-5. This instrument may be used either for making pH determination in the 0-14 pH range, or for millivolt measurements. Temperature corrections can be made manually with a Temperature Adjust-

Fig. 3-2. Fisher Jumo-Size Magnetic Stirrer

Fig. 3-3. International Clinical Centrifuge, Model CL

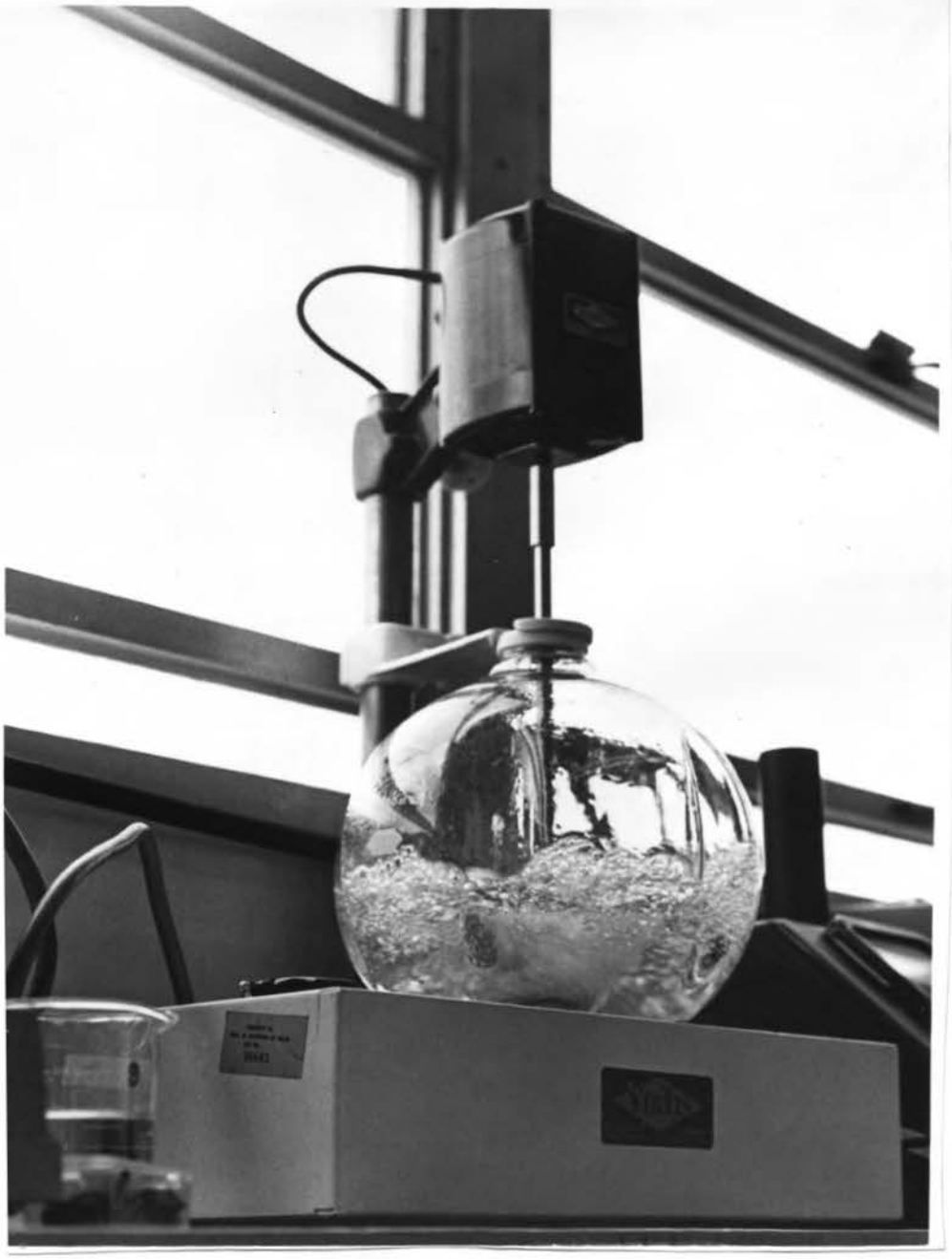


Fig. 3-4. VirTis Aero-Seal Chemixer

Fig. 3-5. Beckman Zeromatic pH Meter

ment Control.

For the pH measurement, this instrument has an accuracy of 0.1 pH unit and a reproducibility of 0.02 unit. Prior to use the instrument was standardized with a buffer solution having a pH of 6.86.

CHAPTER IV

PRELIMINARY SUPPLEMENTAL TESTS

Prior to the experimental studies on the sorption and desorption of pesticides by clay minerals, several supplemental tests were conducted in an attempt to provide a better knowledge about the property, nature and behavior of the experimental materials or facility. These tests included evaluations of (A) properties and behavior of the experimental pesticides in aqueous system, (B) nature of the experimental clay minerals, (C) mixing capacity of the Fisher jumbo-size magnetic stirrer, and (D) the effect of the carrier solvent acetone on the adsorption reaction.

The undertaking of the above preliminary tests were necessary to support the subsequent major experiments for the adsorption study in such a way that certain suitable experimental controls could be provided. Also, the results obtained from these preliminary tests would be helpful in the analysis and explanation of the adsorption data.

A. Properties and Behavior of the Experimental Pesticides in Aqueous System

The following tests were made for the evaluation of some properties and behavior of the experimental chlorinated hydrocarbon pesticides: 1.) determination of efficiency of liquid-liquid extraction of pesticides from aqueous solutions, 2.) determination of the aqueous solubilities of pesticides, and 3.) evaluation of volatilization of pesticides in aqueous system. The procedure and results of each of the above tests are discussed below.

1. Determination of Efficiency of the Liquid-Liquid Extraction of Pesticides from Aqueous Solutions: The aqueous solubilities of the three experimental pesticides, i.e., DDT, dieldrin and heptachlor, are on the order of

parts per billion. Trace quantities of these pesticides present in water can not be accurately measured without the use of some sophisticated instrument such as gas chromatograph. For this research program all measurements of pesticide concentrations were made by using a Varian Aerograph Gas Chromatograph, Model 1520-1B, employing an electron capture detector. This instrument has been previously described in Chapter III (p. 25); the detail of the gas chromatographic analysis of chlorinated hydrocarbon pesticides is also included in the Appendix I.

Because the use of the electron capture detector would not permit direct injection of aqueous pesticide solution into the gas chromatograph, the aqueous pesticide solution must be first extracted with a certain solvent such as hexane and the extract was then subjected to gas chromatographic analysis.

In order to measure accurately the concentration of pesticides present in water sample, a proper procedure for the liquid-liquid extraction of pesticides from aqueous solution must be followed; also the efficiency of this extraction procedure must be determined. A good extraction procedure seems to be one which not only has a high extraction efficiency, but also has a consistent efficiency at all time.

Tests were conducted to find a proper extraction procedure and its efficiency. Variables considered in these extraction tests included the amount of solvent used for extraction, or the volume ratio between the extraction solvent and the aqueous pesticide solution, the length of extraction time, and the manner of extraction.

In a preliminary extraction test, an aqueous dieldrin solution of 100 ppb was prepared from dilution with distilled water of a 100 ppm dieldrin-acetone standard stock solution. A measured volume of this

aqueous dieldrin solution was placed in a separatory funnel which was next added with a certain amount of the solvent hexane. The mixture in the separatory funnel was gently shaken manually for a certain length of time. Thereafter, the hexane extract was collected in a test tube, which was then placed on a 60°C warm water bath to evaporate the hexane and concentrate the pesticide residue; and a carbon-filtered air stream was passed through the mouth of the test tube to aid the rate of hexane evaporation. After the hexane was completely evaporated, a volume of two milliliters of fresh hexane was added to the test tube to redissolve the pesticide residue; and an aliquot of two microliters was injected into the gas chromatograph.

The results of the preliminary extraction test are shown in Table 4-1. From this table, it appears that the extraction efficiencies were unusually low, being in the range between zero to 38 per cent, and were not subjected to the influence of either the length of extraction time or the amount of hexane used for extraction. After the preliminary extraction test, it was speculated that some of the pesticides extracted by hexane could be lost during the step of evaporating the solvent to concentrate the pesticide residue over the warm water bath. Therefore, a second extraction test was conducted in the same manner as the preliminary one except that the evaporation of hexane was eliminated. The extract collected from the separatory funnel was injected directly into the gas chromatograph. The data of this second extraction test are shown in Table 4-2. The results obtained from the second extraction test disclosed that the 100 ppb dieldrin present in water could be extracted completely by hexane solvent, the extraction efficiency being in the range between 90 to 127 per cent. The variation of the efficiency was believed to be due to the experimental errors. The second extraction test also showed that the extraction efficiencies were not

Table 4-1

Results of the Preliminary Extraction Efficiency Test*

Order of Sample	Volume of Aqueous Solution Used for Extraction (ml)	Volume of Hexane Used for Extraction (ml)	Ratio of Hexane: Aqueous Solution	Length of Extraction Time (min.)	Extraction Efficiency (%)
1	25	5	1:5	5	22
2	25	5	1:5	10	22
3	25	5	1:5	20	14
4	25	5	1:5	30	6
5	25	5	1:5	60	0
6	50	5	1:10	5	18
7	50	5	1:10	10	30
8	50	5	1:10	20	25
9	50	5	1:10	30	25
10	50	5	1:10	60	25
11	50	10	1:5	5	34
12	50	10	1:5	10	35
13	50	10	1:5	20	35
14	50	10	1:5	30	27.5
15	50	10	1:5	60	37.5
16	100	5	1:20	5	32.5
17	100	5	1:20	10	20
18	100	5	1:20	20	12.5
19	100	5	1:20	30	38
20	100	5	1:20	60	12.5

* Extractions were made with hexane on an aqueous dieldrin solution of 100 ppb; the hexane extract was concentrated before gas chromatographic analysis.

Table 4-2

Results of the Second Extraction Efficiency Test*

Order of Sample	Volume of Aqueous Solution Used for Extraction (ml)	Volume of Hexane Used for Extraction (ml)	Ratio of Hexane: Aqueous Solution	Length of Extraction Time (min.)	Extraction Efficiency (%)
1	25	5	1:5	2	90
2	25	5	1:5	4	96
3	50	5	1:10	2	100
4	50	5	1:10	4	110
5	30	5	1:6	2	100
6	30	5	1:6	4	100
7	20	5	1:4	2	95
8	20	5	1:4	4	97.5
9	50	10	1:5	2	100
10	50	10	1:5	4	100
11	10	2	1:5	2	125
12	10	2	1:5	4	125
13	20	4	1:5	2	106
14	20	4	1:5	4	108
15	20	2+2**	1:5	2	112
16	20	2+2**	1:5	4	108
17	20	3	1:6.7	2	127
18	20	3	1:6.7	4	127

* Extractions were made with hexane on an aqueous dieldrin solution of 100 ppb. The hexane extract was subjected to gas chromatographic analysis directly without prior concentration.

** Extraction was made twice, each with 2 ml solvent.

substantially affected by the variation of the length of extraction time, the volume of extraction solvent, or the number of extraction. Comparing the data shown in Tables 4-1 and 4-2, it is evident that in the preliminary extraction test, significant amounts of dieldrin were lost with hexane during the step of evaporating the solvent to concentrate the pesticide residue.

After the second extraction test, it was proposed that all the pesticide extractions in the subsequent experiments would be performed by extracting 20 ml of aqueous pesticide solution with four ml of hexane for a period of two minutes. A final extraction test was made to evaluate the extraction efficiencies more thoroughly of the proposed procedure on the aqueous solutions of dieldrin, DDT, and heptachlor, each of which had a pesticide concentration of 100 ppb. For each pesticide solution 10 to 20 samples were extracted each time in the same manner. The results of the final extraction test are listed in Tables 4-3, 4-4, and 4-5. In these tables, the standard deviations of the efficiencies for each pesticide extraction are also included.

The data obtained from the final extraction test revealed that the extraction efficiency for dieldrin was approximately 98 per cent, with a standard deviation of 8.8 per cent.

The extraction efficiencies for both DDT and heptachlor were relatively low, being on the order of 50 per cent, as compared to that for dieldrin; however, the efficiencies were found to be rather consistent as reflected by the low standard deviation, which were approximately two and three per cent, respectively, for DDT and heptachlor. Therefore, proper compensation factors for the extraction efficiency should be applied for DDT and heptachlor in the final calculation of the aqueous pesticide concentration.

Table 4-3

Results of the Final Extraction Efficiency Test*--

From Aqueous Dieldrin Solution

Order of Sample n	Extraction Efficiency N (%)	$N-\bar{N}$	$(N-\bar{N})^2$
1	83	-15.25	234.0
2	89	-9.25	86.2
3	88	-10.25	102.9
4	112	13.75	190.2
5	108	9.75	96.0
6	100	1.75	3.1
7	102	3.75	14.2
8	107	8.75	77.2
9	110	11.75	139.8
10	110	11.75	139.8
11	98	-0.25	0.6
12	98	-0.25	0.6
13	102	3.75	14.2
14	100	1.75	3.1
15	103	4.75	22.8
16	89	-9.25	86.2
17	88	-10.25	102.9
18	89	-9.25	86.2
19	89	-9.25	86.2
20	100	1.75	3.1
Avg. $(\bar{N}) = \Sigma N/n = 98.25$		$\Sigma (N-\bar{N})^2 = 1489.3$	

Standard Deviation $= \sqrt{\Sigma(N-\bar{N})^2/(n-1)} = \sqrt{1489.3/(20-1)} = 8.8\ \%$

* All extractions were performed by extracting 20 ml of 100 ppb aqueous dieldrin solution with four ml of hexane for a period of two minutes.

Table 4-4

Results of the Extraction Efficiency Test*--

From Aqueous DDT Solution

Order of Sample n	Extraction Efficiency N (%)	$N-\bar{N}$	$(N-\bar{N})^2$
1	54	0.8	0.64
2	52	-1.2	1.44
3	52	-1.2	1.44
4	52	-1.2	1.44
5	50	-3.2	10.24
6	57	3.8	14.44
7	54	0.8	0.64
8	52	-1.2	1.44
9	54	0.8	0.64
10	55	1.8	3.24
Avg. $(\bar{N}) = \sum N/n = 53.2$			$\sum (N-\bar{N})^2 = 35.60$

Standard Deviation $= \sqrt{\sum (N-N)^2/(n-1)} = \sqrt{35.60/(10-1)} = 1.99$ %

* All extractions were performed by extracting 20 ml of 100 ppb aqueous DDT solution with four ml of hexane for a period of two minutes.

Table 4-5

Results of the Extraction Efficiency Test*--

From Aqueous Heptachlor Solution

Order of Sample n	Extraction Efficiency N (%)	$N-\bar{N}$	$(N-\bar{N})^2$
1	50	1.5	2.25
2	50	1.5	2.25
3	49	-2.5	6.25
4	49	-2.5	6.25
5	50	1.5	2.25
6	49	-2.5	6.25
7	54	2.5	6.25
8	56	4.5	20.25
9	52	0.5	0.25
10	56	4.5	20.25
Avg. $(\bar{N}) = \Sigma N/n = 51.5$			$\Sigma (N-\bar{N})^2 = 72.50$

Standard Deviation $= \sqrt{\Sigma(N-\bar{N})^2/(n-1)} = \sqrt{72.50/(10-1)} = 2.84$ %

* All extractions were performed by extracting 20 ml of 100 ppb aqueous heptachlor solution with four ml of hexane for a period of two mintues

2. Determination of the Aqueous Solubilities of Pesticides: Although in the literature the aqueous solubilities of DDT and dieldrin had been reported (20,47), the solubility values were not consistent among the different investigators. This is primarily due to the different pesticide samples used and the different experimental procedure employed in the solubility determination. The determinations of the aqueous solubilities of the experimental pesticides are necessary in estimating the maximum concentration of these pesticides being able to retain in the liquid solution. Therefore, a test was undertaken to determine the aqueous solubilities of DDT, dieldrin and heptachlor at three different temperature levels, 10°C, 20°C and 30°C.

The test procedure for the pesticide solubility determination involved the addition of an excessive amount of a certain pesticide into a VirTis aero-seal chemixer glass flask containing three liters of distilled water; the content in the flask was next blended in a high speed for a period of three hours, and the solution was passed through a millipore filter having a pore size of 0.45 micron to filter out insoluble pesticide particles. The concentration of pesticide in the filtrate was then determined.

The results of the pesticide solubility determinations are shown in Table 4-6. Some of the aqueous solubilities of the pesticides evaluated in these tests are not in agreement with those reported by other investigators. For example, the solubility of DDT was reported to be 40 ppb when the maximum particle size allowed in water was 5 microns (47); however, DDT was found to have a solubility ranging from 88 to 145 ppb at temperature between 10 and 30°C, when the maximum particle size allowed was 0.45 microns. Another example is the solubility of dieldrin, which was reported to be in the range of 100 to 205 ppb at temperatures between 10 and 30°C (20),

Table 4-6

Aqueous Solubilities of the Experimental Pesticides

Pesticide	Pesticide Solubility (ppb) in water at Temperature of		
	10°C	20°C	30°C
DDT	88	130	145
Heptachlor	23	29	48
Dieldrin	9.5	40	105

whereas the dieldrin solubility observed in these tests was only approximately one half of the above reported values. The discrepancies between the data obtained in these tests and those by other investigators may, as being pointed out before, be due to the different pesticide samples used and the different experimental procedures employed in the solubility determinations. For instance, most of the DDT samples are composed of o,p'- and p,p'-isomers; of these, the o,p'-isomer has a much larger aqueous solubility than its p,p'-derivative. Therefore, a DDT sample having a larger percentage of o,p'-isomer would accordingly have a higher aqueous solubility.

3. Evaluation of Volatilization of Pesticides in Aqueous System: In the literature it has been reported that pesticides can be lost in the field by direct volatilization into the air. In the earlier extraction study described in this Chapter, it was found that dieldrin could be lost with hexane during the step of evaporating hexane solvent to concentrate the pesticide residue. Therefore, it was speculated that a substantial amount of chlorinated hydrocarbon pesticides might be lost from the test solution in the subsequent adsorption experiment. Tests were conducted to investi-

gate the loss of experimental pesticides from aqueous solutions in different kinds of containers, including one-liter graduated cylinder, four-liter widemouth Pyrex glass bottle and 10-gallon glass aquarium, at different properly designed environmental conditions such as varied pH, temperature and salt content of the aqueous solution. The following paragraphs will summarize briefly the volatilization tests and their results.

a.) Volatilization of dieldrin from aqueous solutions with varied pH in one-liter graduated cylinders: In this test three liters of 100 ppb aqueous dieldrin solution were prepared from dilution with distilled water of a 100 ppm dieldrin-acetone stock standard. One liter of the aqueous pesticide solution was then placed in each of the three graduated cylinders of one-liter capacity and the pH was adjusted to 2.0, 4.0 and 6.0, respectively, with 0.1 N hydrochloric acid. These graduated cylinders were then placed in the 23 $\pm$ 1°C air-conditioned laboratory for a test period of four days and the concentrations of dieldrin in the graduated cylinders were measured at frequent intervals in order to determine the loss of the pesticide. The results of this test are shown in Table 4-7 and Fig. 4-1.

The data shown in Fig. 4-1 disclosed that the rate of volatilization of dieldrin from aqueous solutions were affected by the pH of the solutions. The volatilization of dieldrin was reduced by decreasing the pH of the solution. As shown in Table 4-7, after four days of standing, the aqueous dieldrin solutions of 100 ppb contained in the one-liter graduated cylinders were reduced to 77, 70 and 60 ppb, respectively, when the pH of the solutions were 2.0, 4.0 and 6.0.

b.) Volatilization of heptachlor from aqueous solution in one-liter graduated cylinder: The test for the volatilization of heptachlor was also conducted in the same manner as described above for the dieldrin test

Table 4-7

Volatilization of Dieldrin from Aqueous Solutions with Varied pH in One-Liter Graduated Cylinders

Time of Standing	Concentration of Dieldrin Remaining (ppb)		
	pH 2.0	pH 4.0	pH 6.0
0 hr.(initial)	100.0	100.0	100.0
1 "	89.5	87.0	80.0
3 "	74.5	84.5	68.5
5 "	80.0	81.5	69.0
1 day	78.5	79.5	67.0
1½ "	77.5	86.0	67.0
2 "	70.0	78.5	68.0
2½ "	61.5	76.5	68.0
3 "	70.0	73.5	63.5
4 "	77.0	70.0	60.0

Table 4-8

Volatilization of Heptachlor from Aqueous Solution* in One-Liter Graduated Cylinder

Time of Standing (days)	Concentration of Heptachlor Remaining (ppb)
0 (initial)	100
2	70
3	49
4	36
6	28
7	17
9	11
10	12
12	5
14	4

* The initial 100 ppb aqueous heptachlor solution had a pH of 6.8.

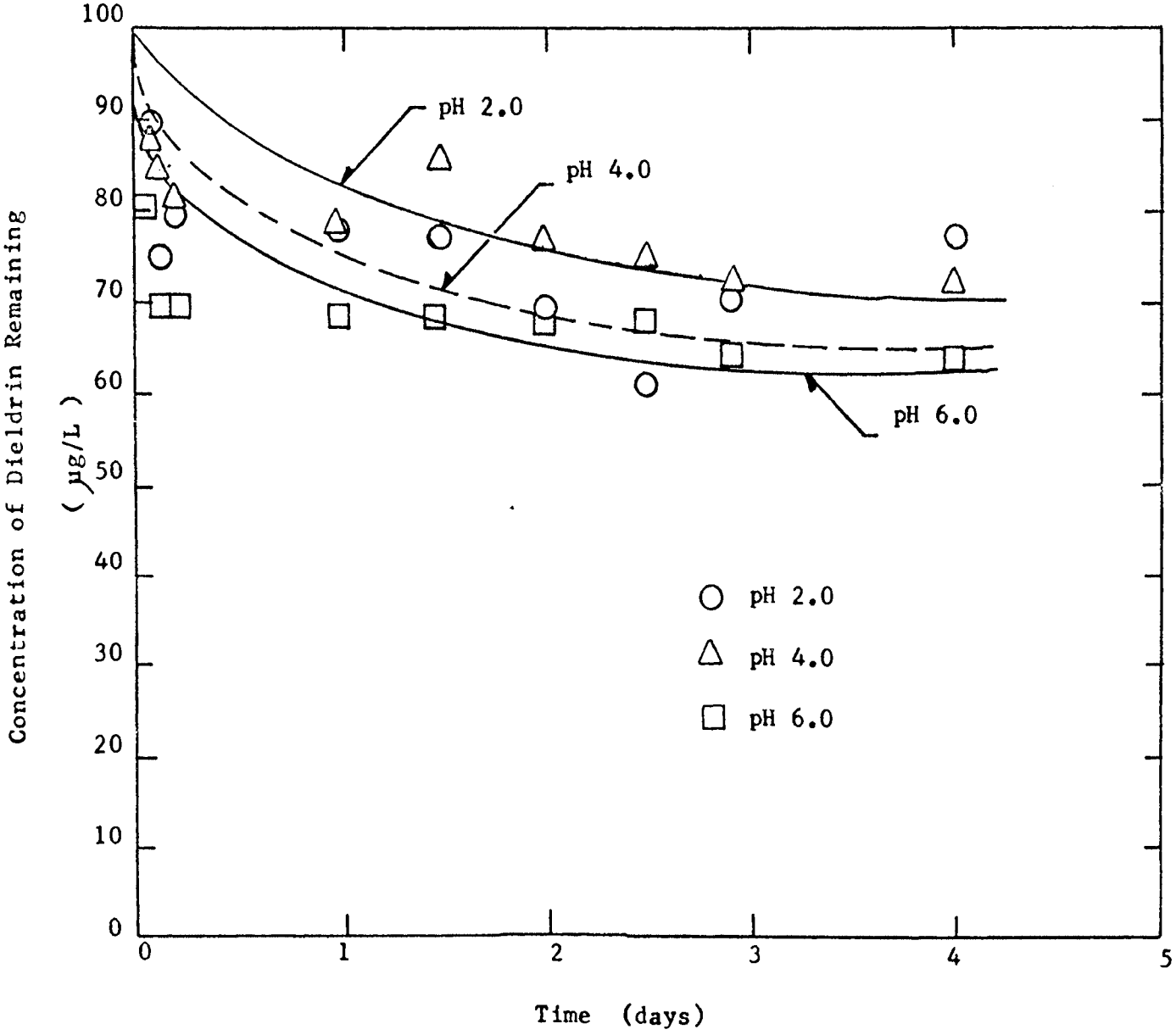


Fig. 4-1. Volatilization of Dieldrin from Aqueous Solution in Graduated Cylinders

except for a longer test period of 14 days. The results of this test, shown in Table 4-8 and Fig. 4-2, indicated that the volatilization of heptachlor was almost twice as much as that of dieldrin after four days of standing. At the end of the 14-day test period, there was only 4 ppb of pesticide remaining in the test solution.

c.) Volatilization of pesticides from aqueous solutions in the four-liter widemouth Pyrex glass bottles: Tests were made to evaluate the volatilization of the experimental pesticides from aqueous solutions contained in the four-liter widemouth Pyrex glass bottles, which were used as the reaction chamber in the subsequent batch studies of the adsorption reaction. (see Chapters V and VI).

For each test, six liters of an aqueous pesticide solution were prepared from the 100 ppm pesticide-acetone stock standard. The pesticide solution was next dispensed equally into two widemouth Pyrex glass bottles, one of which was capped and the other uncapped in order to determine the difference in their rates of volatilization. The pesticide solution in these two bottles were continuously agitated by Fisher jumbo-size magnetic stirrers for a test period of 11 hours. During each test, samples were withdrawn at frequent time intervals and the concentration of pesticides were determined. The results of these tests are shown in Table 4-9 and Fig. 4-3.

Results obtained from these tests revealed that the rates of volatilization of pesticides generally increased in the following:

$$\text{DDT} < \text{Dieldrin} < \text{Heptachlor}.$$

There were no significant loss of DDT from the aqueous solutions during the test period regardless if the bottle was capped or not. The volatilization of dieldrin was moderate; approximately 10 per cent of dieldrin was

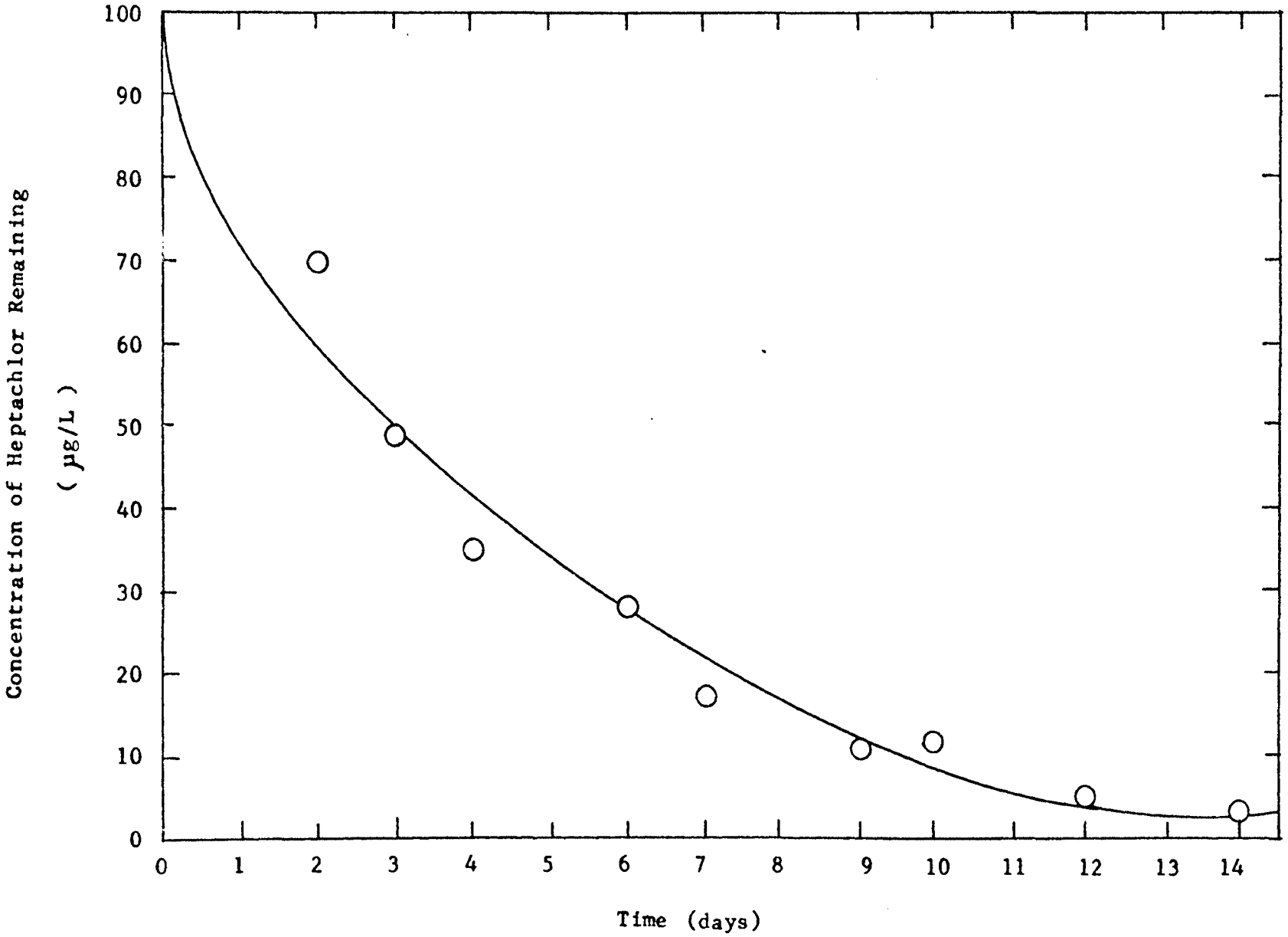


Fig. 4-2. Volatilization of Heptachlor from Aqueous Solution in Graduated Cylinder

Table 4-9

Volatilization of Pesticides from Aqueous Solutions in the Four-Liter Widemouth Pyrex Glass Bottles*‡

Time of Standing (hrs.)	Concentration of Pesticides Remaining (ppb)					
	DDT		Dieldrin		Heptachlor	
	closed cap	open cap	closed cap	open cap	closed cap	open cap
0 (initial)	100	100	100	100	100	100
½	100	100	108	94	97	100
1	98	97	94	100	98	87
1½	98	96	104	97	99	90
2	99	98	99	92	95	73
3	97	96	128	91	102	65
5	102	98	113	90	110	60
7	103	102	120	97	92	43
11	98	97	115	89	86	32

* The pesticide solutions in the bottles were continuously agitated by Fisher jumbo-size magnetic stirrers.

‡ Parallel tests were made with both capped and uncapped bottles.

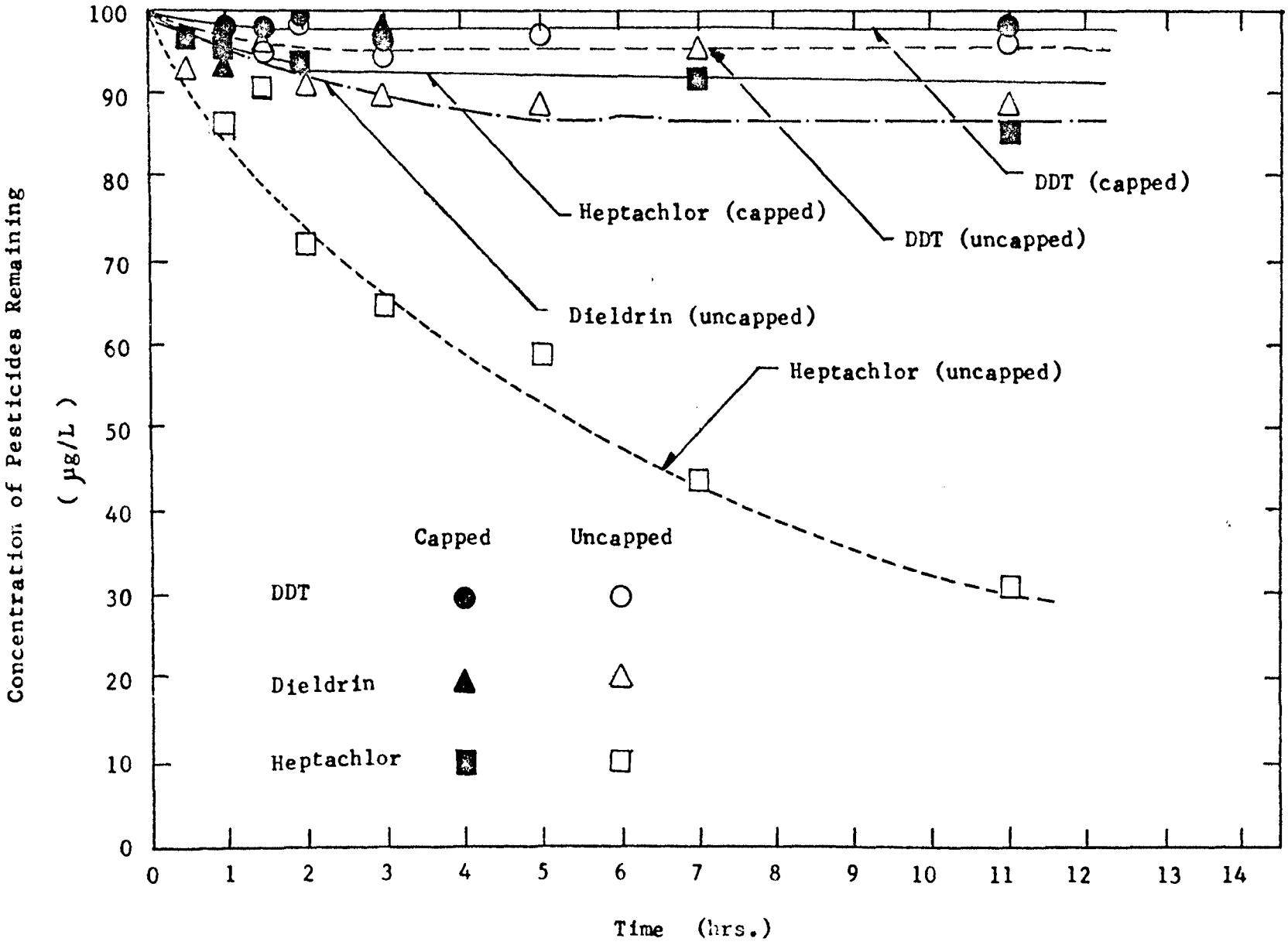


Fig. 4-3. Volatilization of Pesticides from Aqueous Solutions in Widemouth Bottles

lost at the end of the 11-hour test period when the test bottle was not capped; however, with the test bottle capped, there was no loss of dieldrin at all. Unlike DDT or dieldrin, heptachlor appeared to volatilize significantly from the aqueous solutions. At the end of the test, the concentration of heptachlor remaining was 86 ppb in the capped test bottle and only 32 ppb in the uncapped one.

d.) Volatilization of dieldrin from aqueous solutions with varied pH, temperatures and salt concentrations in 10-gallon glass aquaria: Further tests were performed to determine the loss of dieldrin from aqueous solutions in 10-gallon aquaria under the effect of certain different environmental conditions such as varied pH, temperatures and salt (NaCl) concentrations. These tests were made because in the subsequent sorption and desorption study (see Chapter VII), experiments were conducted in these 10-gallon glass aquaria under the aforementioned environmental stresses.

In these tests, pH of the pesticide solutions were varied at 6.0, 8.0, and 10.0, temperatures at 10°C, 20°C and 30°C, and salt concentrations at 0.03, 0.3 and 3.0 per cent.

In each separate test only one environmental factor was evaluated for its effect on the volatilization of dieldrin. A volume of 2.5 gallons of 100 ppb aqueous dieldrin solution was placed in each of three glass aquaria. These aquaria and the pesticide solutions were then adjusted to or controlled under the intended environmental conditions and the concentrations of dieldrin remaining in the solutions were determined at frequent intervals throughout a test period of 72 hours.

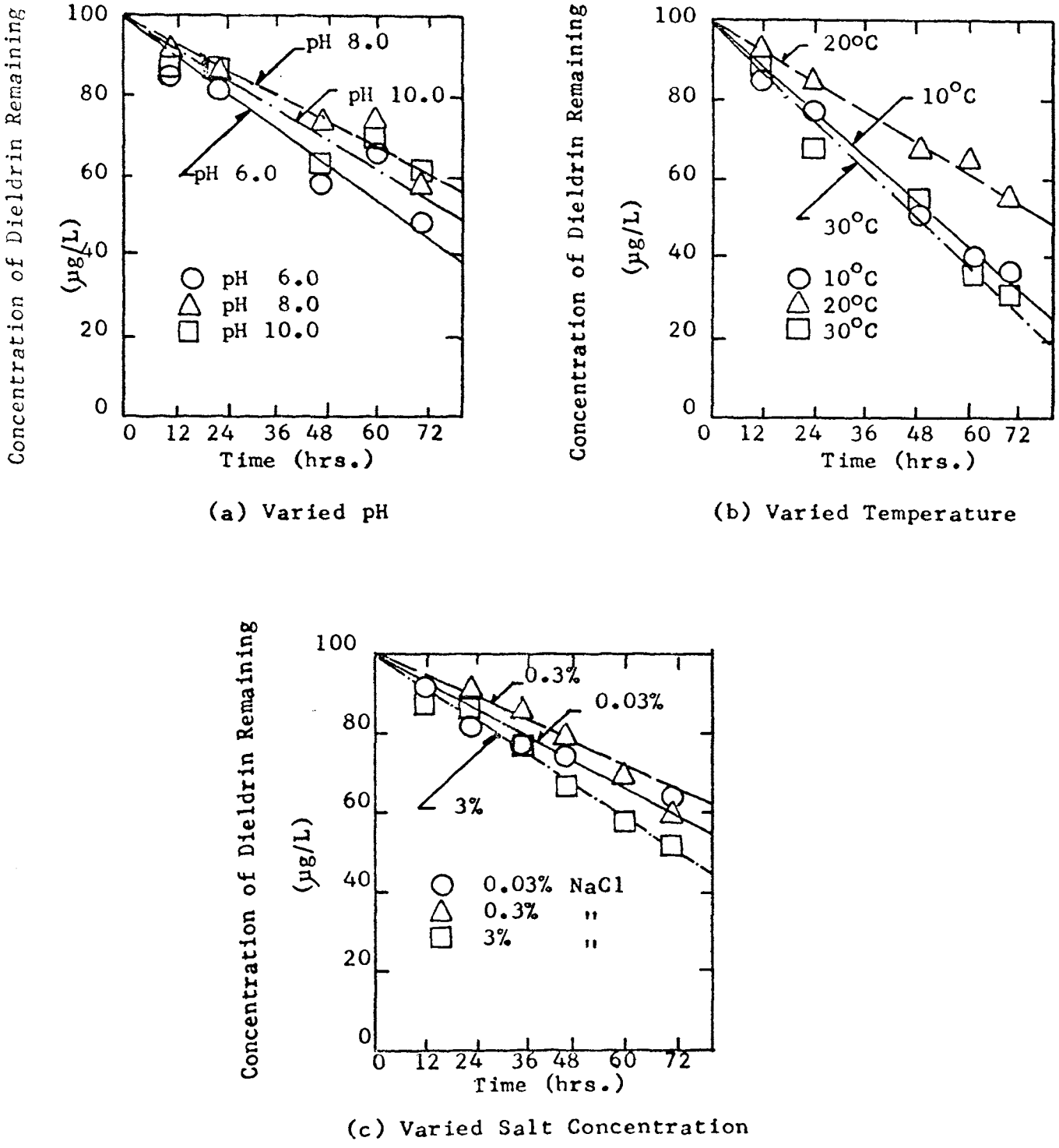
The results of these tests, as shown in Table 4-10 and Fig. 4-4, disclosed that the volatilization of dieldrin was affected by the three environmental factors evaluated. For example, the rate of loss of dieldrin

Table 4-10

Volatilization of Dieldrin from Aqueous Solutions

in 10-Gallon Glass Aquaria

Time of Standing (hrs.)	Concentration of Dieldrin Remaining (ppb)								
	pH			Temperature			Salt Concentration(%)		
	6.0	8.0	10.0	10°C	20°C	30°C	0.03	0.3	3.0
0 (initial)	100	100	100	100	100	100	100	100	100
½	-	-	-	99	96	96	102	102	101
1	100	105	105	87	98	92	107	106	103
1½	105	105	102	93	98	99	106	101	100
2	110	102	102	100	99	96	91	100	92
3	102	92	97	95	102	95	101	107	101
5	104	111	91	94	99	96	99	102	103
7	103	91	98	93	96	99	100	97	101
12	86	91	87	84	93	83	93	106	91
24	80	81	83	78	87	68	80	88	82
36	-	-	-	-	-	-	83	84	75
48	57	75	61	49	64	56	73	77	63
48½	65	66	66	48	69	50	68	74	68
49	52	70	79	45	59	51	73	73	61
49½	83	87	75	48	63	51	67	69	69
50	74	74	74	48	64	49	61	70	67
51	76	78	73	48	63	46	65	68	67
52	69	76	74	42	68	41	68	65	65
55	74	69	69	41	68	37	68	64	63
60	66	73	77	39	64	36	65	64	59
72	48	58	60	37	56	34	62	58	53



(a) Varied pH

(b) Varied Temperature

(c) Varied Salt Concentration

Fig. 4-4. Volatilization of Dieldrin from Aqueous Solutions in Glass Aquaria

seemed to be higher in a solution having a pH of 6.0 than to either acidic or alkaline range, as indicated in Figs. 4-1 and 4-4a. The loss of the pesticide was slower at 20°C than at either 10 or 30°C, Fig. 4-4b; however, no good reasons are available to explain these observations. The salt concentration of water appeared to exert only slight effects on the rate of pesticide volatilization. A variation of 100 fold in aqueous salt concentrations, i.e., 0.03 vs. 3.0 per cent, resulted in only less than 10 per cent difference in the amounts of dieldrin lost, Fig. 4-4c.

B. Nature of the Experimental Clay Minerals

The clay minerals employed in this study were obtained from natural field pits. These clay materials were properly prepared and sieved in the laboratory before experiment, as described in Chapter III (p. 23), in an attempt to obtain samples of uniform particle-size in the adsorption study. However, the organic material, if any, present in the clay samples would not be affected by such treatment. Since many investigators (6,14,20) reported that the organic content of a soil sample would exert significant effects on the adsorption of organic pesticides by the soil, a test was conducted to determine the organic concentration of the experimental clays. The pH of aqueous clay suspensions at different solid concentrations were also determined.

The organic contents of the three experimental clay materials were evaluated by three different approaches: the Wet-Combustion Total Carbon Test (1), the conventional COD Test (53) and the Volatile Solid Test (53). The Total Carbon Test (TCT) was performed in the Soil Mechanics Laboratory, Department of Civil Engineering, University of Missouri-Rolla. The detailed procedure for this Total Carbon Test is described in the Appendix II. The

results of the organic content determinations are shown in Table 4-11. The pH of aqueous clay suspensions at different solid concentrations are shown in Table 4-12.

From Table 4-11, it is clear that all the three experimental clays contained only traces of organic matter as reflected by the TCT and COD Test. It must be pointed out here that the relatively high values for the volatile solid concentrations shown in this table were not due to the organic matter contained in the clays, but due to the loss of water content from the clay minerals during the baking of these clays in a 600°C muffle furnace. Therefore, the volatile solid determination can not be used to estimate the organic content of a clay sample.

The pH measurement of the aqueous clay suspensions revealed that the kaolinite and illite clay suspensions were acidic in nature while the montmorillonite clay suspension was slightly basic when the solid concentrations were more than 0.05 per cent.

C. Mixing Capacity of the Fisher Jumbo-Size Magnetic Stirrers

At the planning stage of this research program, it was proposed that the evaluation of the rate of uptake of pesticides by clay minerals would be conducted in several four-liter widemouth Pyrex glass bottles; and the mixtures of clay-pesticide suspension would be continuously agitated by using Fisher jumbo-size magnetic stirrers, which have been described in Chapter III (p. 28). The maximum clay concentration which could be used in the subsequent adsorption study would be limited by the mixing capacity of the magnetic stirrers. Therefore, tests were made to evaluate the maximum mixing capacity of these stirrers.

In these tests several clay suspensions with different solid concen-

Table 4-11

Organic Contents of the Experimental Clays Materials

Type of Clay	Organic Content		
	Total Carbon Test (mg CO_2/g clay)	COD (mg/g clay)	Volatile Solids (mg VS/g clay)
Kaolinite	0.37	0.32	1340
Illite	0.64	1.80	465
Montmorillonite	1.60	1.57	695

Table 4-12

The pH of Aqueous Clay Suspensions

Type of Clay	pH at the Solid Concentration of				
	10%	1.0%	0.1%	0.05%	0.01%
Kaolinite	4.7	5.4	6.5	6.7	7.0
Illite	4.6	5.2	5.5	5.8	5.8
Montmorillonite	8.5	8.0	7.4	7.0	6.8

trations,up to 20 per cent by weight, were prepared and placed in the four-liter glass bottles. The content in the bottles were mixed by Teflon-coated stirring bars operated by the jumbo-size magnetic stirrers. Visual observations were made to check if the stirring bar could mix the clay suspensions; also, samples of 25 ml each were randomly pipetted from different locations within the bottle and analyzed for their solid concentrations. If a uniform solid concentration observed in all samples taken from the same bottle, it would be a sign of a sufficient mixing. From these tests, it was found that the Fisher jumbo-size magnetic stirrers were sufficient to mix thoroughly a clay suspension with a solid concentration up to 15 per cent; when the clay concentration was increased to 20 per cent, the movement of the stirring bar appeared to be somewhat sluggish and the clay suspension could not be uniformly mixed. Therefore, in the subsequent adsorption studies, the maximum clay concentration employed was limited to 10 per cent in order to ensure that a proper mixing could be obtained at all time.

D. The Effect of the Carrier Solvent Acetone on the Adsorption Reaction

In Chapter III (p. 24) it has been mentioned that because of some difficulties encountered in dispersing the experimental pesticides directly in water, all aqueous pesticide solutions used in the adsorption study were prepared by using acetone as the carrier solvent. However, before undertaking the adsorption study it was questioned if the use of acetone as the carrier solvent would impart any effect on the uptake of pesticides by the experimental clays. To clear up this uncertainty, a study was undertaken to compare the difference in the uptakes of dieldrin by kaolinite from aqueous pesticide solutions prepared in different manners. One of the pesticide solutions was prepared by dispersing dieldrin directly in water

using a VirTis aero-seal chemixer as described in Chapter III (p. 28), while the other was prepared using acetone as a carrier solvent, i.e., from the dilution with distilled water of a 100 ppm dieldrin-aceton stock solution. The results obtained from this study disclosed that the use of acetone as the pesticide carrier exerted no substantial effects either in the rate of uptake or in the equilibrium of adsorption. Therefore, in the later adsorption study acetone was used as the carrier solvent for the preparation of the pesticide solutions.

CHAPTER V

BATCH STUDIES OF ADSORPTION--RATES OF UPTAKES

A series of experimental studies were conducted to evaluate the uptake rates of DDT, dieldrin, and heptachlor by the three experimental clay minerals, i. e., kaolinite, illite and montmorillonite, under laboratory controlled conditions.

A. General Procedure

The rate studies were conducted in a series of four-liter capacity widemouth Pyrex glass bottles, in which solutions were agitated with Teflon-coated stirring bars operated by Fisher jumbo-size magnetic stirrers, Fig. 5-1. These bottles were sealed with ground-glass stoppers during each test in order to prevent the volatilization of the test pesticides. The rate studies were conducted in an air-conditioned laboratory, where the temperature was maintained at $23 \pm 1^{o}C$.

Two runs of experimental studies employing slightly different procedures were conducted for the evaluation of the rates of uptakes of pesticides by clay minerals. In the first run of the uptake studies, a volume of two liters of the clay-distilled water mixture, having varied concentrations of clay solids was placed in each of the reaction bottles; the mixture in each bottle was agitated by a magnetic stirrer for a couple of minutes before the additional one liter of aqueous pesticide solution at a concentration of 300 µg/l was added to the bottle. The fate of pesticide was then determined at frequent time intervals until an equilibrium stage was reached. The above procedure was undertaken in an attempt to prepare a final pesticide concentration of 100 µg per liter of clay suspension. The results obtained from this first run of the uptake rate studies, which are

Fig. 5-1. Experimental Setup for the Study on Rate of Uptake

included in Appendix III, indicated that a very strong adsorption of pesticides took place within seconds of reaction; yet, in many cases substantial amounts of the adsorbed pesticides were gradually desorbed and released into the water phase in order to maintain an equilibrium state. The observed phenomenon of the initial strong adsorption of pesticides followed by the gradual desorption was attributed to the fact that when the one liter of aqueous pesticide solution of 300 µg/l was added to the clay suspension, some of the clay particles might be immediately in direct contact with the pesticide molecules and adsorb them before these molecules were further dispersed in the liquid medium. Because of the high solute concentration present in the 300 µg/l pesticide solutions, a large quantity of pesticides could be adsorbed initially. As the reaction time passed, some of the adsorbed pesticide molecules would be gradually desorbed from the clays and released into water in order to maintain a final equilibrium state between the liquid and the solid phases.

Because of the substantial desorption of pesticides observed in the first run of the uptake rate study a second run of this study was conducted with a slightly modified procedure. In the second run, a quantity of three liters of pesticide solution at a concentration of 100 µg/l was first placed in each of the reaction vessels. Then predetermined amounts of clay were added to the pesticide solution and the fate of pesticide was determined. During each test samples were withdrawn from the test system at frequent intervals and the residual pesticide concentrations in water were determined by means of gas chromatographic analysis. The detailed procedure for the gas chromatographic analysis of chlorinated hydrocarbon pesticides is included in the Appendix I.

B. Results and Discussion

The data of the second experimental run of the uptake rate studies are tabulated in the Appendix IV, and are presented in the subsequent figures. Results obtained from this rate study revealed that a large quantity of the experimental pesticides could be adsorbed by the test clay minerals within few minutes of reaction. In general, the adsorptions of chlorinated hydrocarbon pesticides on illite and kaolinite were nearly instantaneous whereas the adsorption of these pesticides on montmorillonite was slightly slower. Among the three pesticides studied, DDT appeared to be adsorbed most easily and in the largest quantity, heptachlor was next, and dieldrin adsorbed the least.

Figures 5-2 and 5-3 illustrate the rates of adsorption of DDT on illite and kaolinite, respectively. After two minutes of contact between the pesticide and clay minerals, the concentrations of DDT remaining in the test solutions were reduced from an original level of 100 µg/l to 47 and 57 µg/l in the presence of Q.1 g/l of illite and kaolinite, respectively. In both tests the concentrations of DDT remaining after one hour of reaction were close to their equilibrium levels. Therefore, the adsorptions of DDT on illite and kaolinite were very fast, with a very large portion of the clays' adsorptive capacities being saturated within few minutes of reaction.

On the other hand, the rate of uptake of DDT by montmorillonite, as shown in Fig. 5-4, appeared to be slightly sluggish as compared to the uptake rates by illite and kaolinite. Weber and Gould (63) found that the data obtained from the adsorption of organic pesticides on active carbon could be linearized by plotting the amount of pesticide adsorbed per unit

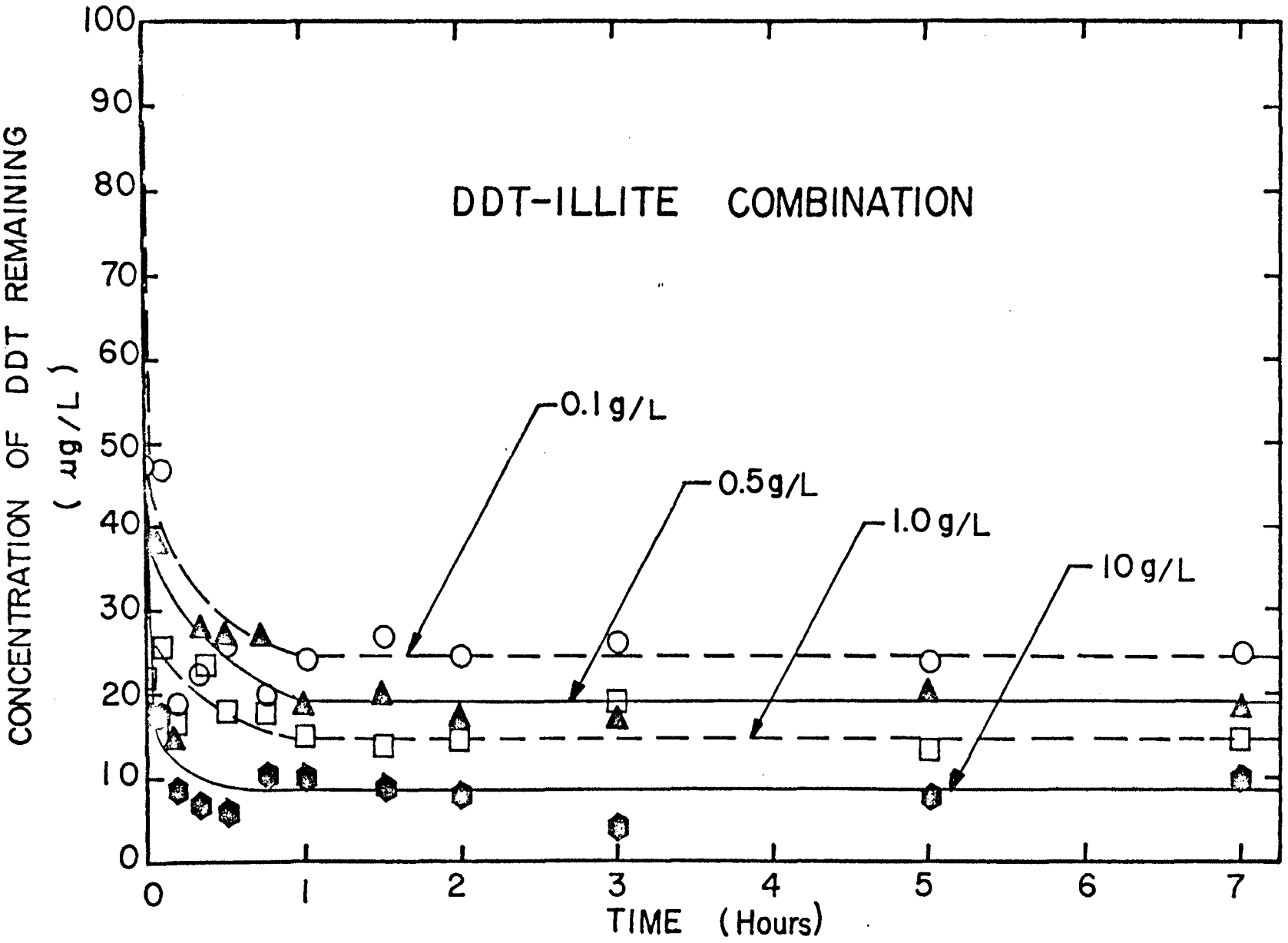


Fig. 5-2. Rate of adsorption of DDT on Illite

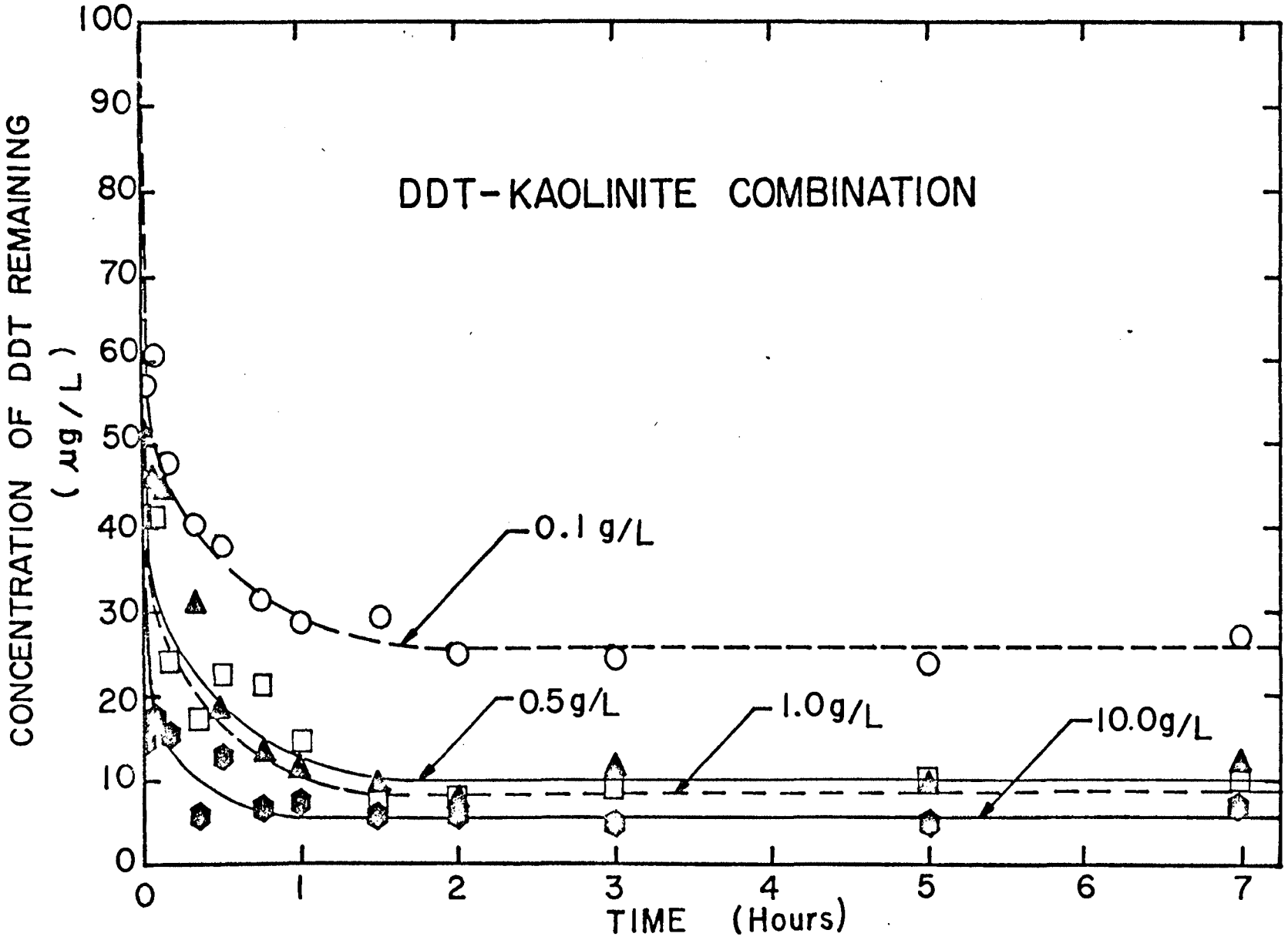


Fig. 5-3. Rate of Adsorption of DDT on Kaolinite

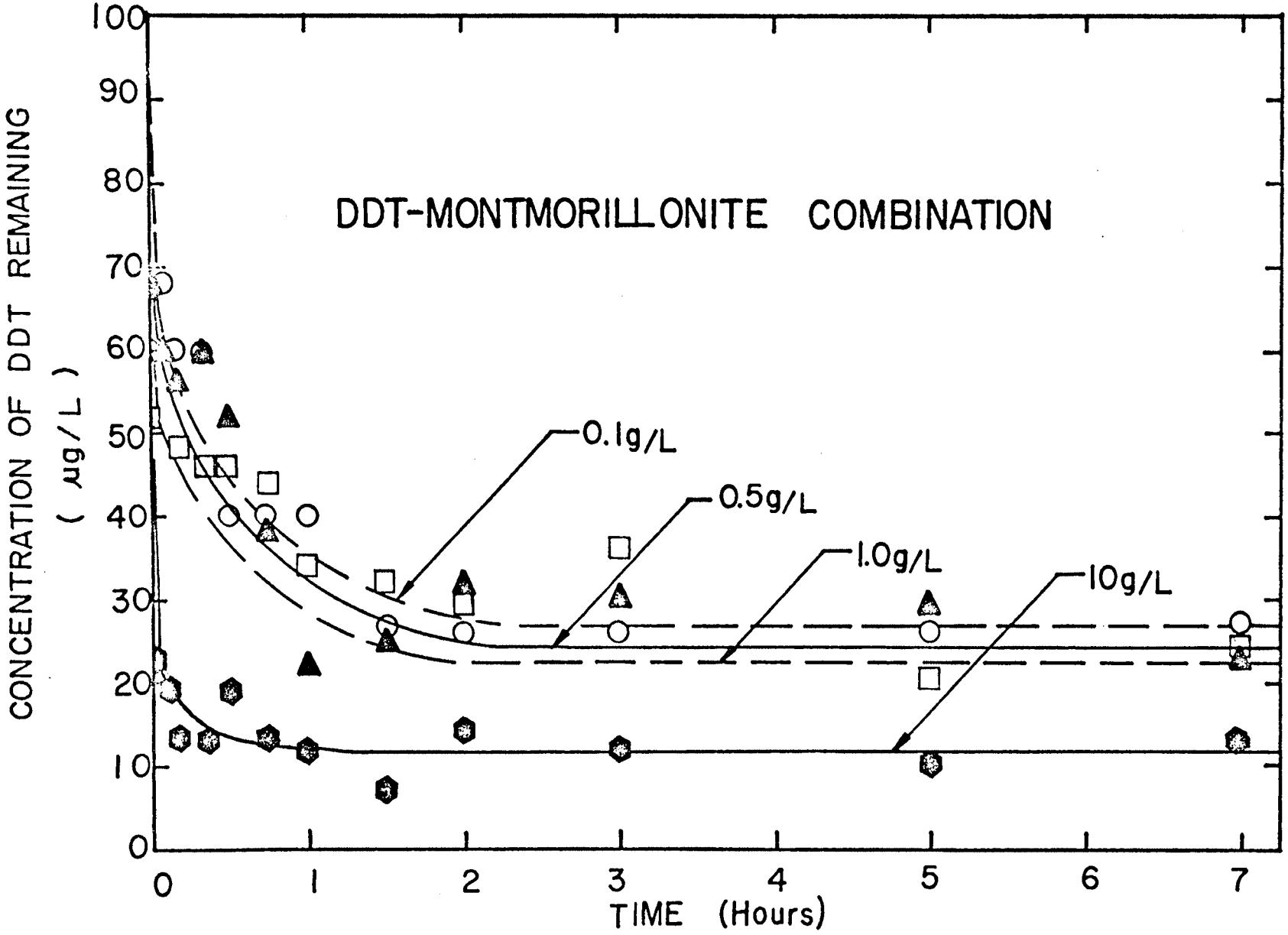


Fig. 5-4. Rate of Adsorption of DDT on Montmorillonite

weight of carbon versus the square root of reaction time, as illustrated in Fig. 5-5. The linearization of these data explains the fact that the rate of uptake of pesticides by active carbon is governed by the intraparticle transport process, a typical behavior controlling the rate of active carbon adsorption. Clays, unlike active carbon, do not possess fine pores and capillaries in the particle physical structure; therefore, in general, the above phenomenon of rate control by intraparticle transport can not be expected in the adsorption of pesticides on clays. Indeed, the uptakes of pesticides by illite and kaolinite were found to be so fast that large quantities of pesticides were adsorbed nearly instantaneously as described previously. However, exceptions were experienced with the adsorption of pesticides on montmorillonite since the rate of uptake by this clay was found to be a gradual progression. One possible reason may be that montmorillonite is an expansible type of clay; in the stacking of the silica-alumina-silica basic units, oxygen layers of each unit are adjacent to the oxygens of the neighboring unit layers with a consequence that there is a very weak bond and an excellent cleavage between them (29). Upon contact with water, the spacings between unit layers of montmorillonite clay can be gradually expanded by entering water and other organic molecules. The diffusion of pesticides into the expanding interlamellar spacings may behave like the intraparticle transport. This explanation would become more evident if Fig. 5-4 is replotted with the concentration of pesticide remaining versus the square root of reaction time, a fairly good linearization of the adsorption data can be obtained, as shown in Fig. 5-6. From this linear plot the adsorption of DDT on montmorillonite clay could be divided into three distinct stages. The first stage was accomplished by the instantaneous adsorption, at which pesticide was deposited on clay particle

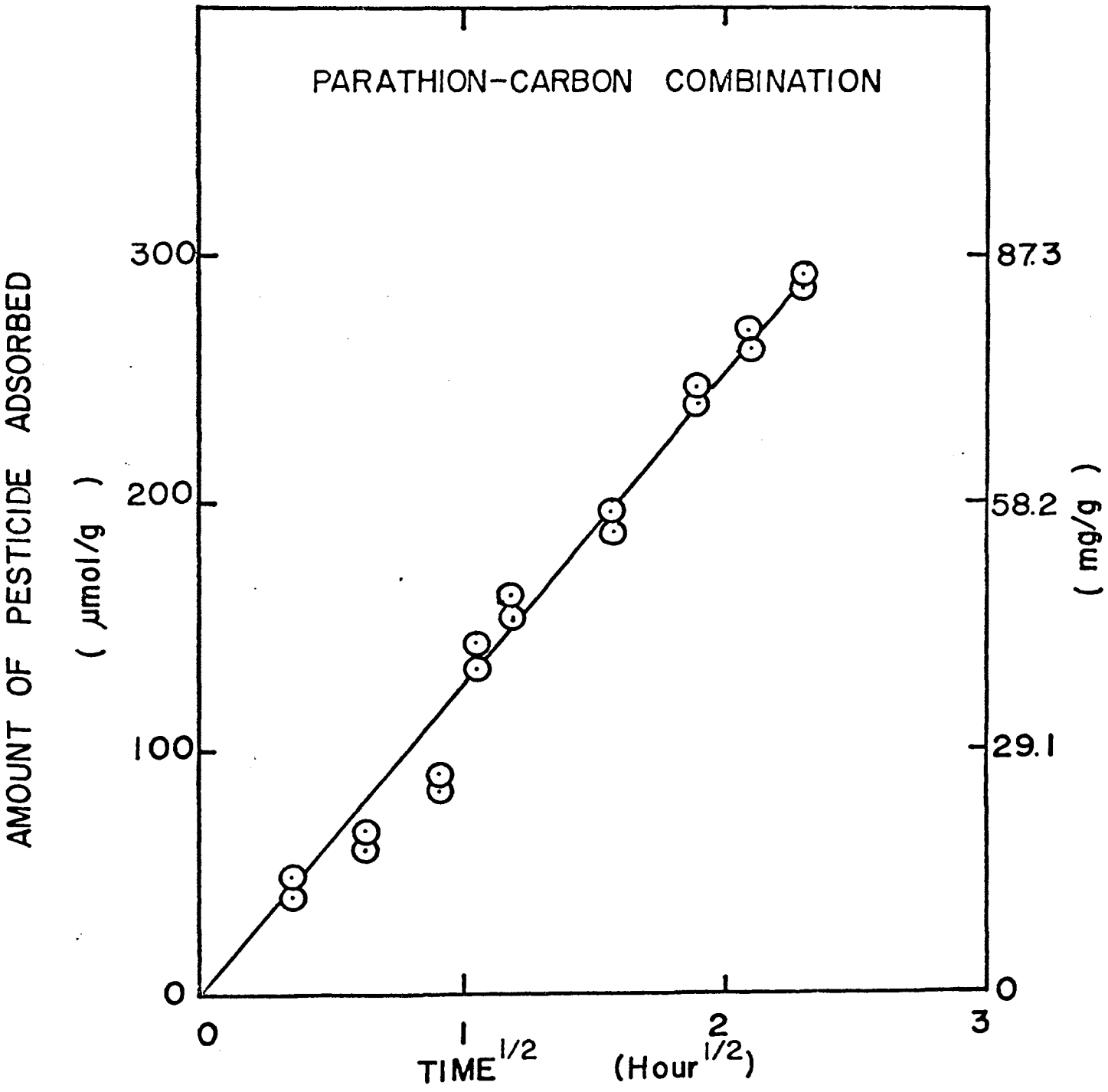


Fig. 5-5. Rate of Adsorption of Parathion on Active Carbon (after Weber & Gould (63))

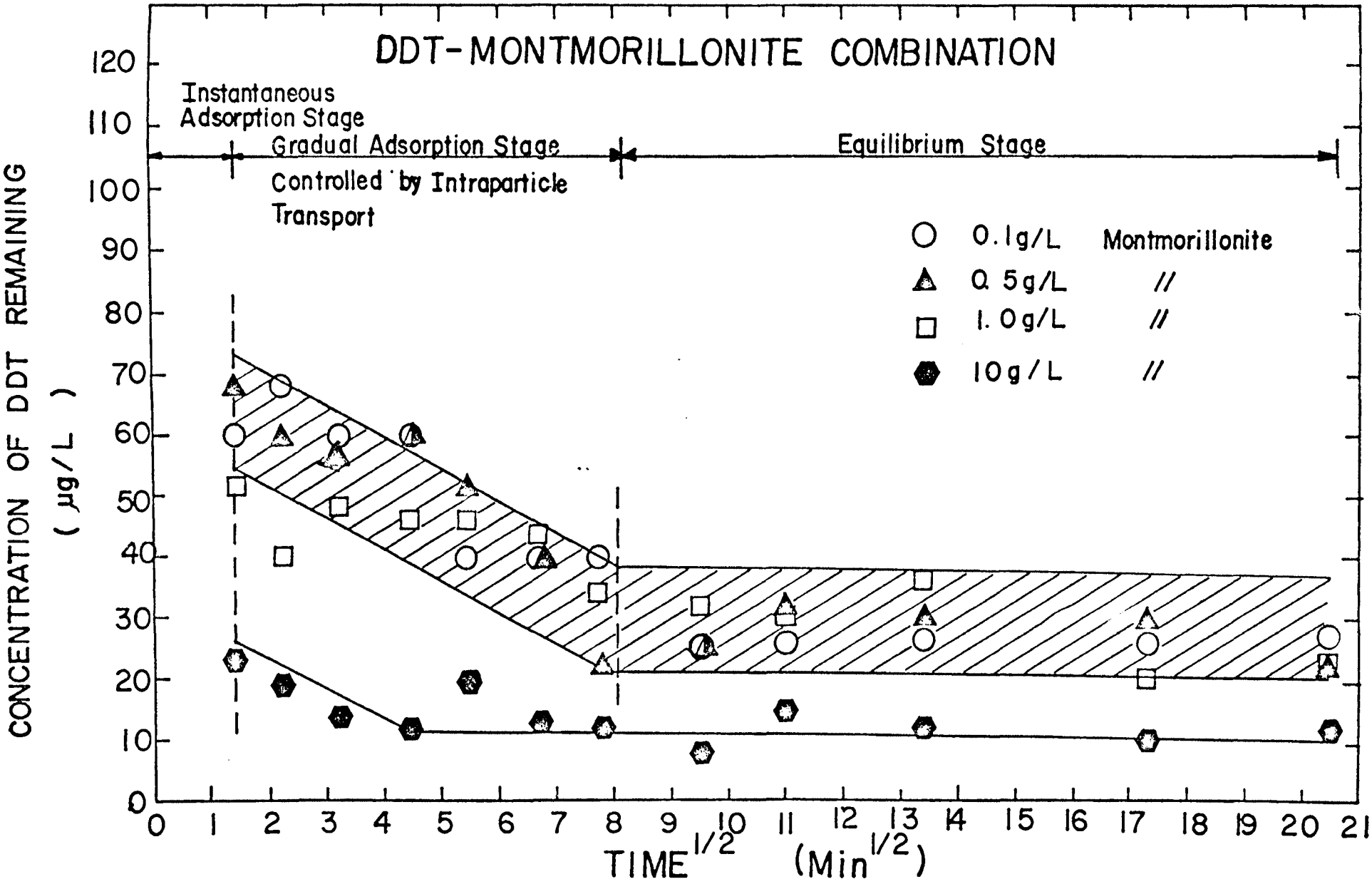


Fig. 5-6. Three Stages of Adsorption of DDT on Montmorillonite

edges or surfaces. The second stage was achieved by gradual adsorption, at which montmorillonite clay was slowly expanded by the diffusing water and pesticide molecules into the interlamellar spacings; the rate of adsorption at this stage was controlled in the same manner as by the intraparticle transport process. The third stage was the final equilibrium, at which no more adsorption of pesticide was observed.

Since illite and kaolinite are non-expansible types of clay, only the instantaneous adsorption stage was observed before reaching the final equilibrium; the second stage of the gradual adsorption by the diffusion of pesticides into the interlayer spacings was not significant.

The rates of adsorptions of heptachlor on different types of clay minerals were found to be much in the same magnitude as compared to those of DDT. As shown in Figs. 5-7 and 5-8, the adsorptions of heptachlor on illite and kaolinite were nearly instantaneous reactions, with the equilibria being reached within few minutes of reaction. On the other hand, the adsorption of heptachlor on montmorillonite was a gradual progression, as shown in Fig. 5-9; the adsorption data as in the case of DDT, can also be linearized into the three distinct adsorption stages, Fig. 5-10.

It is interesting to note the different pattern of the kinetic curves of the adsorption of dieldrin on the test clay minerals, as illustrated in Figs. 5-11, 5-12, and 5-13. Generally speaking, the adsorptions of dieldrin on all experimental clays were instantaneous, and the maximum capacities of adsorption could be reached within few minutes of reaction. Thereafter, gradual desorptions of dieldrin from the clays were observed during the next one hour of reaction, and then the systems approached equilibria. Although the quantities of dieldrin desorbed from the clays were small as compared to the amounts of pesticide already adsorbed, the trend of desorption was

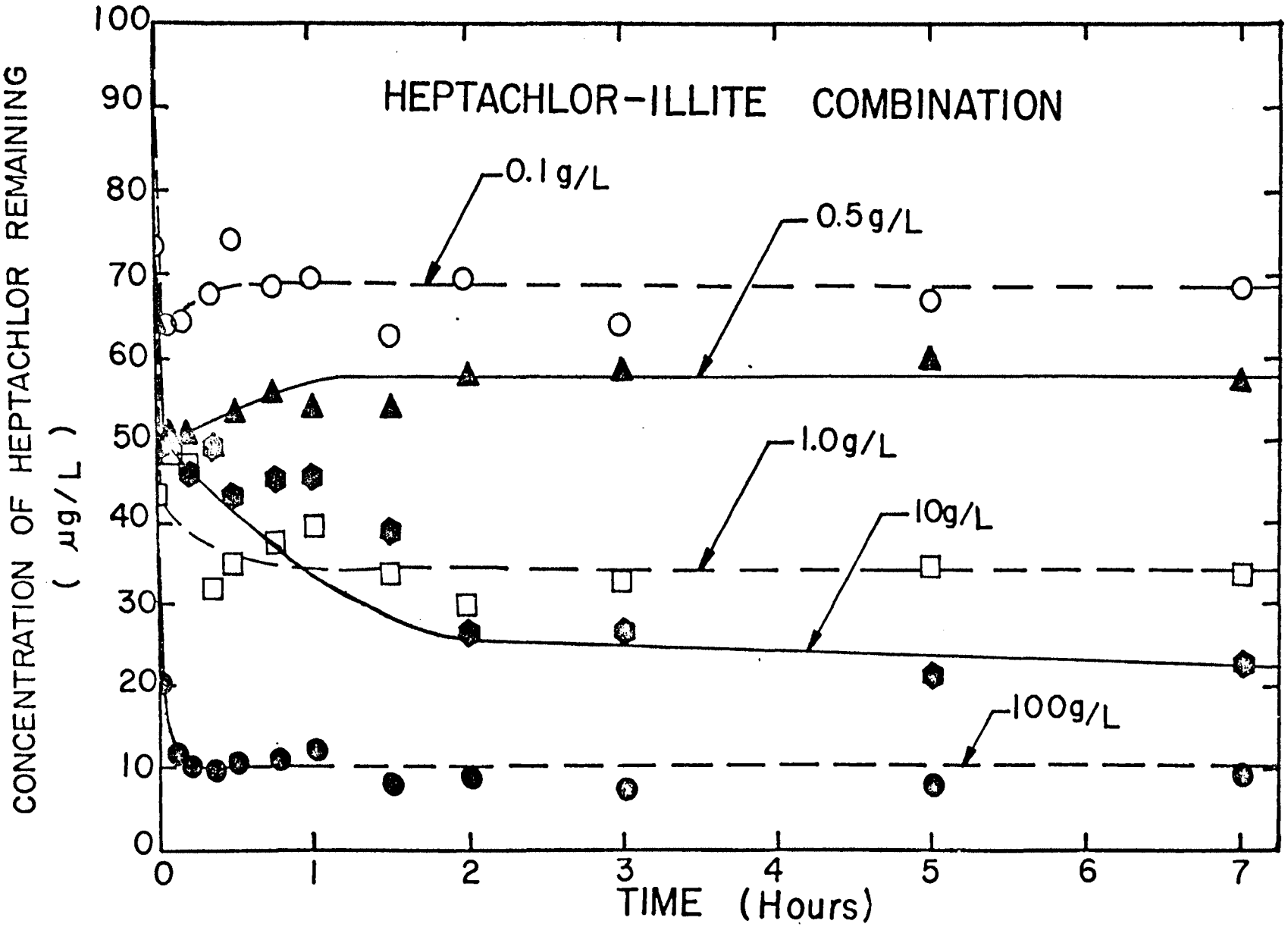


Fig. 5-7. Rate of Adsorption of Heptachlor on Illite

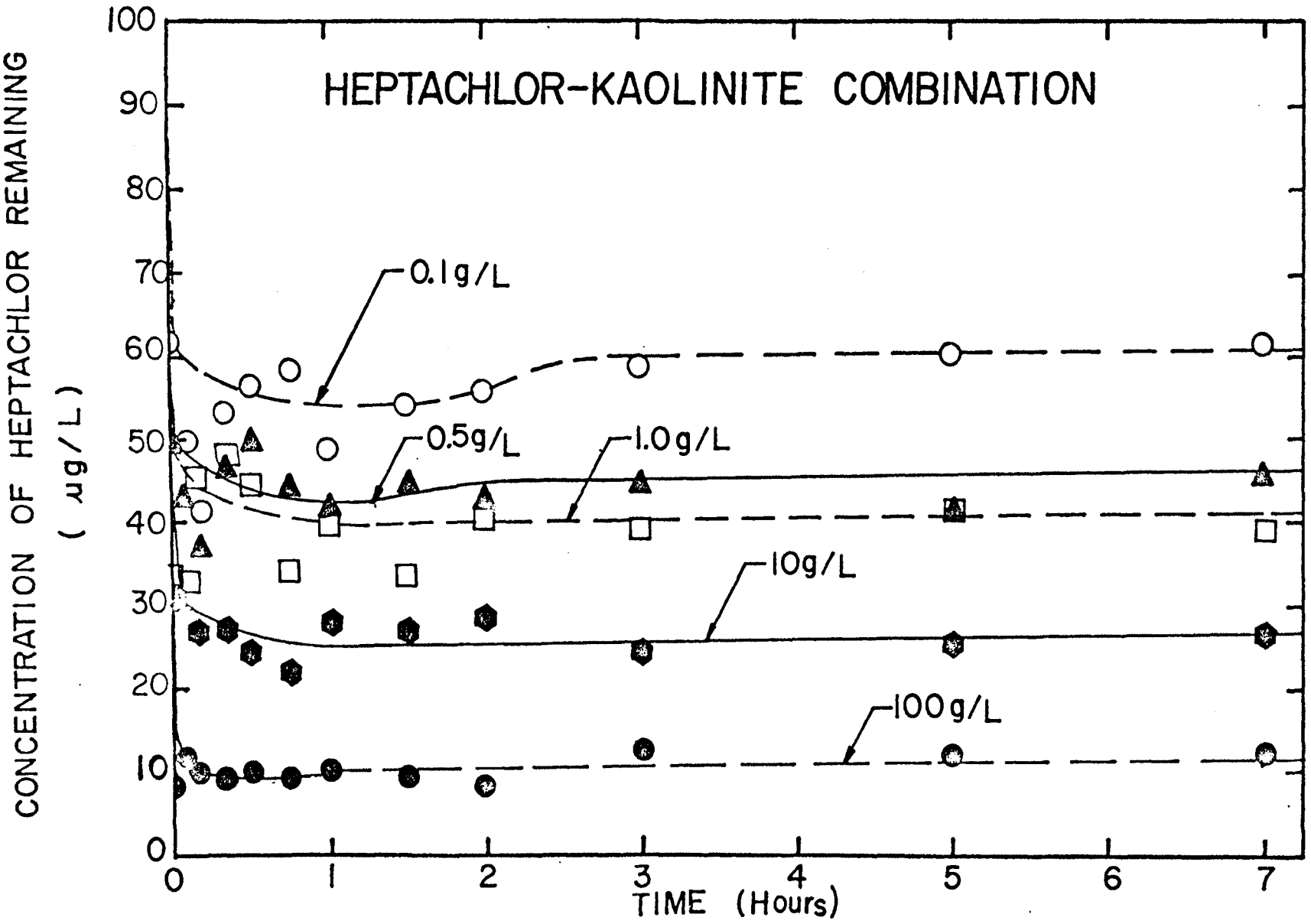


Fig. 5-8. Rate of Adsorption of Heptachlor on Kaolinite

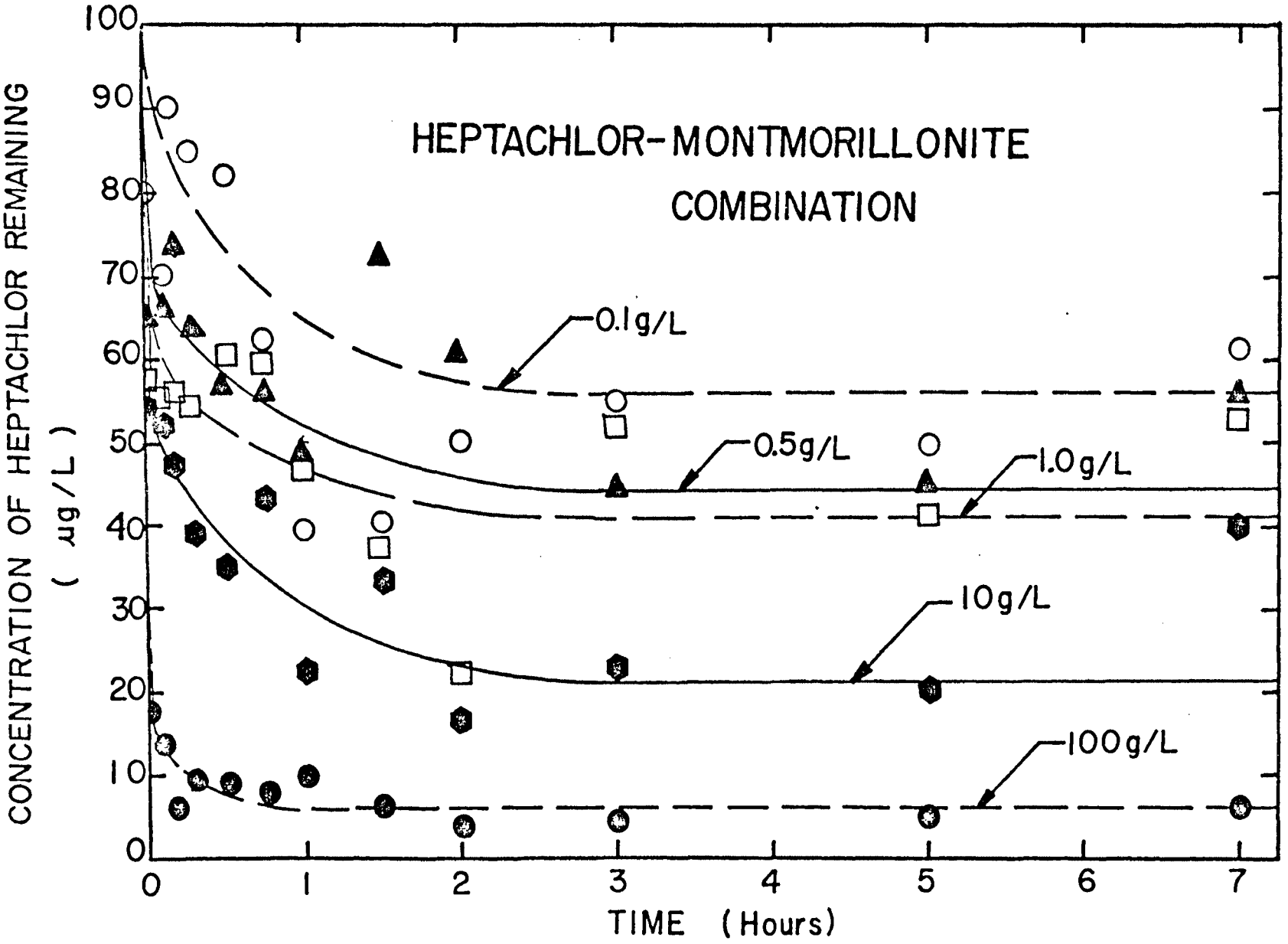


Fig. 5-9. Rate of Adsorption of Heptachlor on Montmorillonite

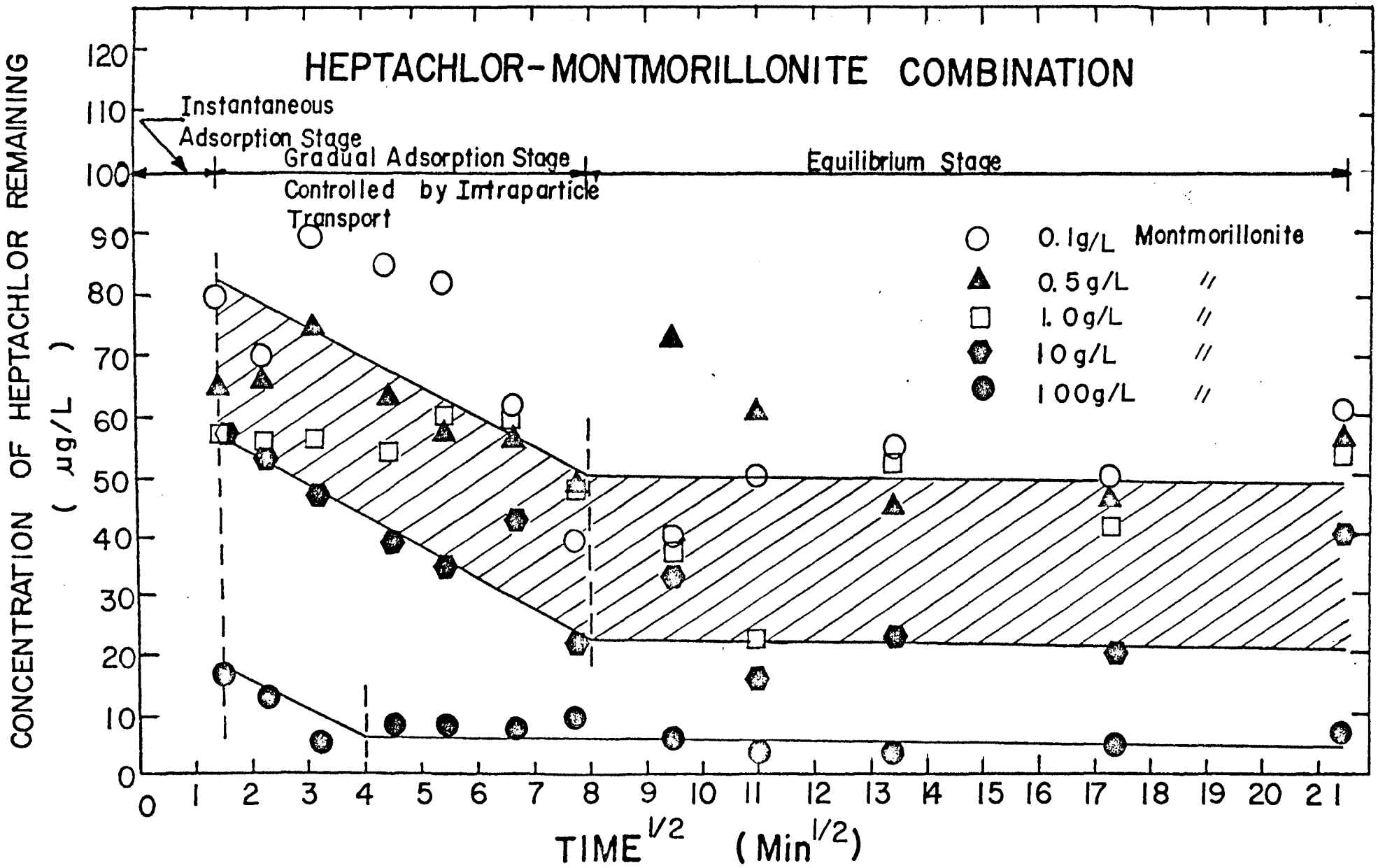


Fig. 5-10. Three Stages of Adsorption of Heptachlor on Montmorillonite

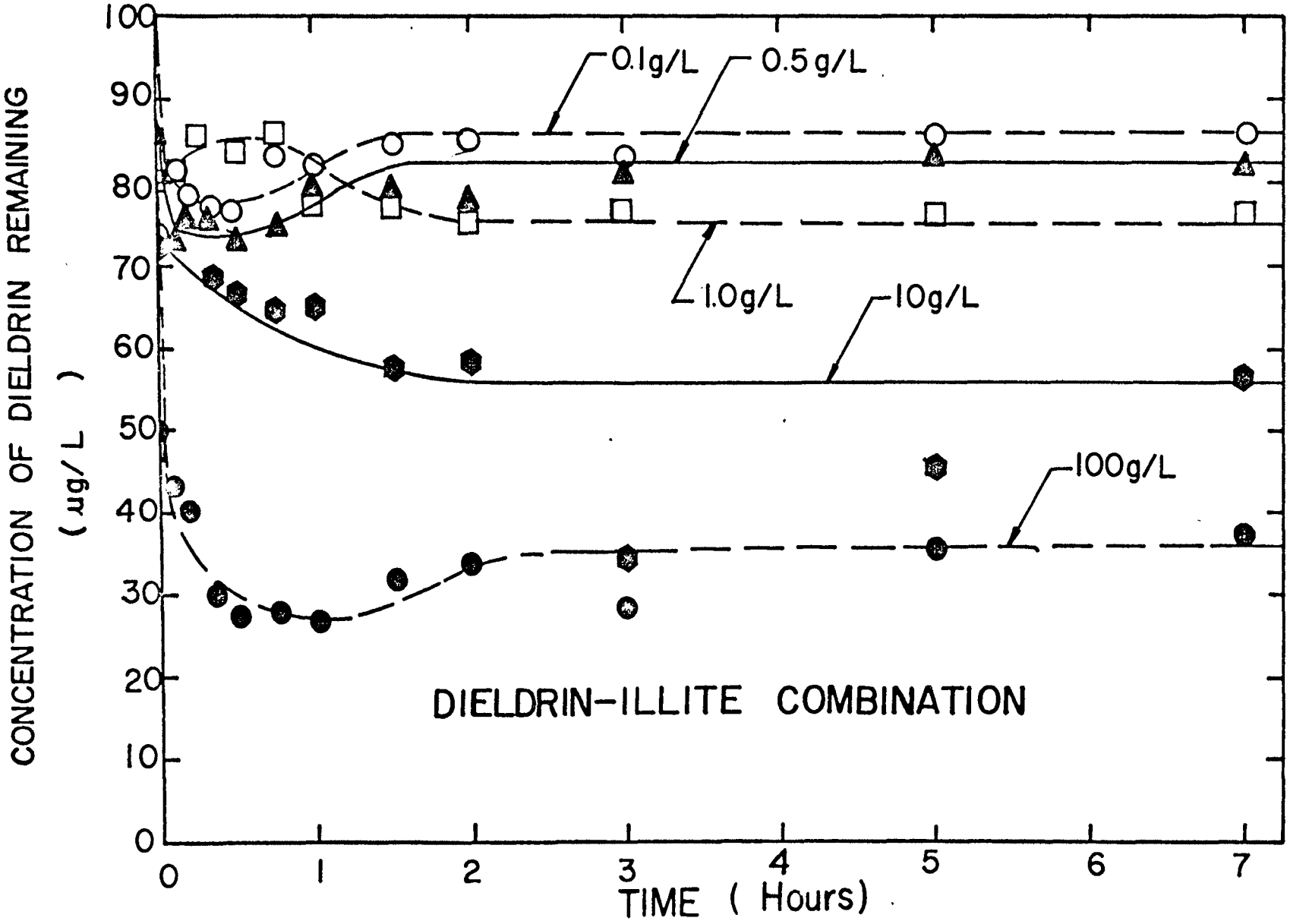


Fig. 5-11. Rate of Adsorption of Dieldrin on Illite

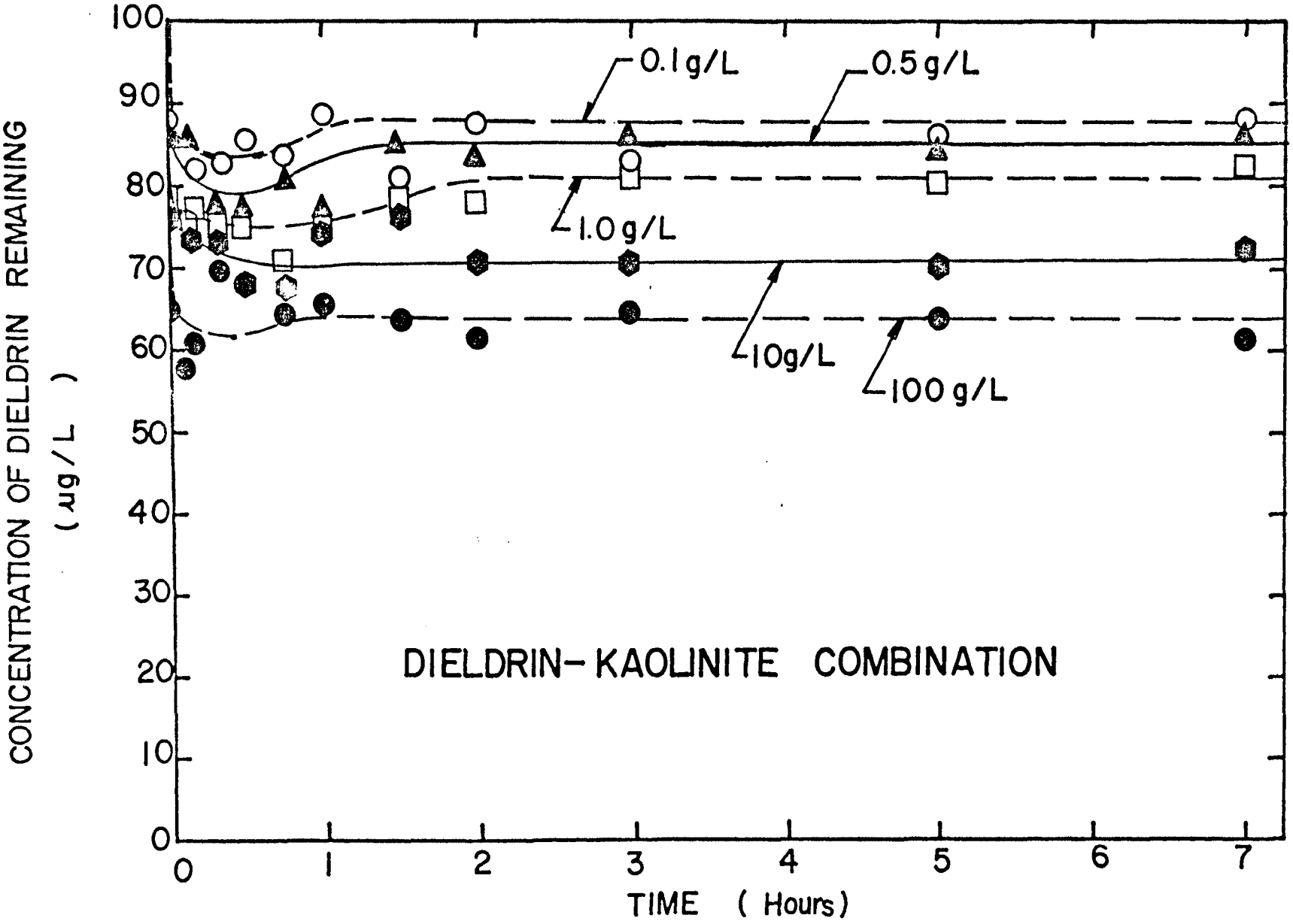


Fig. 5-12. Rate of Adsorption of Dieldrin on Kaolinite

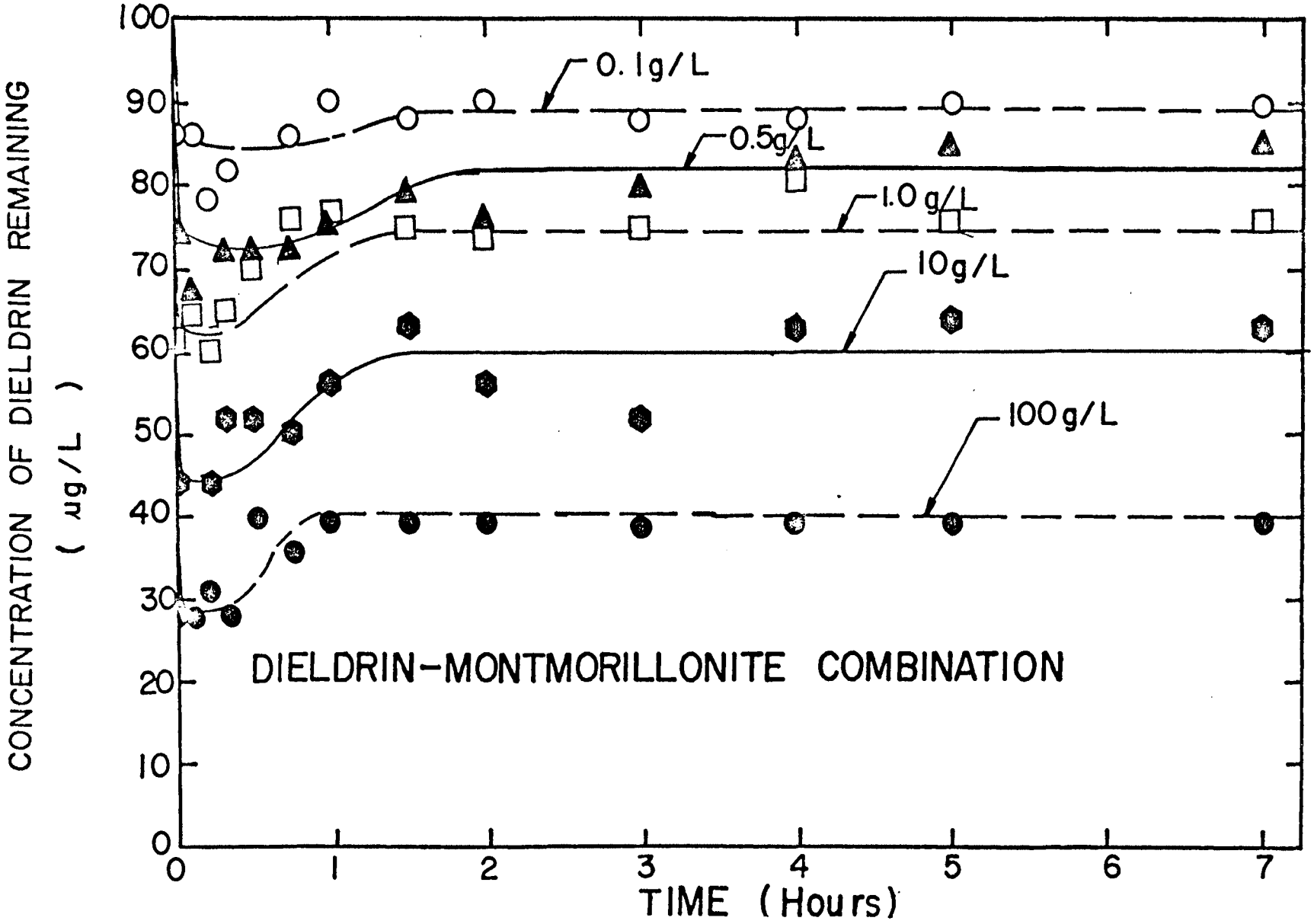


Fig. 5-13. Rate of Adsorption of Dieldrin on Montmorillonite

definite. The extent of desorption was relatively slight in the kaolinite suspension and became more significant in the illite and montmorillonite systems. No good reason is available to explain the possible mechanism which caused this desorption of dieldrin from the experimental clays.

CHAPTER VI

BATCH STUDIES OF ADSORPTION--EQUILIBRIA OF UPTAKES

In all types of adsorption reaction, in general, the amount of solute adsorbed by a fixed quantity of adsorbent depends on the solute concentration remaining in the solution at an equilibrium condition. The position of equilibrium in an adsorption reaction is normally expressed by the adsorption isotherm which relates the quantity of solute adsorbed per unit weight of adsorbent as a function of the equilibrium concentration of solute remaining in the solution.

Perhaps the best way to express quantitatively the adsorption of organic pesticides by clay minerals is to find a mathematical relationship of the adsorption isotherm for the reaction. There are several mathematical models available in the literature (4,21) of adsorption isotherms for different types of reactions. The selection of a certain model will depend on the curve-fit of the experimental data obtained from equilibrium studies. Therefore, experiments were conducted in laboratory to evaluate the adsorption equilibria of various pesticide-clay combined systems.

A. General Procedure

Studies of adsorption equilibria were conducted in a series of 500-ml capacity Erlenmeyer flasks. In each test a volume of 250 ml of an aqueous pesticide solution at a concentration of 100 μg/l was dispensed in each of the flasks which were then added with accurately weighed amounts of the test clay mineral, the weight being varied to cover the range of desirable equilibrium solute concentrations. Each flask was sealed with a rubber stopper wrapped with aluminum foil and the mixture in the flask was agitated

with a magnetic stirrer for a period of five hours before the fate of pesticide was evaluated. From the previous uptake rate studies (see Chapter V) it was found that the time required for reaching an equilibrium state for any of the selected pesticide-clay combinations was less than three hours; so the provision of a 5-hour reaction period was sufficient to ensure that an equilibrium state of the test system should be reached. The temperature for the equilibrium studies was maintained at $23 \pm 1^{\circ}C$, which was the same as for the previous rate studies. The procedure for the gas chromatographic analysis of the pesticides remaining in the test solution is described in the Appendix I.

B. Results and Discussion

The results obtained from the adsorption equilibrium studies are shown in Table 6-1. Detail analyses of these data were made in order to find out with which adsorption isotherm would these experimental data be best fitted. After several tries of curve-fit, it was found that the data from these equilibrium studies conformed fairly well to the Freundlich adsorption isotherm, which has a following mathematical expression:

$$x/m = KC^{1/n} \qquad \text{(Eq. 6-1)}$$

where

x = amount of adsorbate adsorbed at equilibrium condition,
m = weight of adsorbent,
c = concentration of solute remaining at equilibrium condition,
K and n = experimental constants of adsorption isotherm depending upon the specific adsorbent-adsorbate combination and temperature.

The Freundlich isotherm shown in Eq. 6-1 can be rewritten in the following linear form:

Table 6-1. Equilibrium Concentrations of Pesticide Remaining in Various Pesticide-Clay Combination

Pesticide-Clay Combination	Equilibrium Concentration of Pesticide Remaining (ppb) in the Suspension Having a Clay Concentration of											
	0.01 g/l	0.05 g/l	0.1 g/l	0.25 g/l	0.5 g/l	1 g/l	2.5 g/l	5 g/l	10 g/l	50 g/l	100 g/l	200 g/l
DDT-Illite	70.0	49.4	42.4	-	29.2	19.1	-	14.1	10.0	-	-	-
DDT-Kaolinite	44.0	42.0	41.4	-	40.0	24.3	-	22.4	21.6	-	-	-
DDT-Montmorillonite	30.0	28.4	17.3	-	15.6	12.7	-	7.3	4.5			
Heptachlor-Illite	91.5	70.3	69.8	-	64.8	59.8	-	58.5	55.2	-	35.2	17.6
Heptachlor-Kaolinite	61.0	51.0	49.6	-	47.4	40.0	-	29.8	27.8	-	12.8	8.2
Heptachlor-Montmorillonite	82.2	80.0	56.0	-	44.0	40.0	-	23.8	22.4	-	18.1	13.9
Dieldrin-Illite	95.5	92.0	88.6	-	78.2	73.6	-	72.5	70.0	-	52.0	39.0
Dieldrin-Kaolinite	87.0	85.0	85.0	-	81.0	75.0	-	70.0	66.0	-	54.0	52.0
Dieldrin-Montmorillonite	82.0	-	82.0	71.6	73.0	75.0	77.8	77.0	71.6	57.0	45.0	-

$$\log (x/m) = \log K + (1/n) \log C \qquad \text{(Eq. 6-2)}$$

Therefore, by plotting the values of x/m and C on log-log paper, the experimental data can be linearized if the type of adsorption relationship conforms to the Freundlich model. From the linear plot the adsorption constants of K and 1/n can be determined. Almost all the adsorptions of the experimental pesticides on clay minerals at the state of equilibrium are in reasonable accord with the Freundlich adsorption isotherm. Plots for these isothermal adsorption equilibria for various pesticide-clay combinations are shown in Figs. 6-1, 6-2 and 6-3; the slope of the straight line in each plot represents 1/n, and the value of K can then be determined by using Eq. 6-2. The experimental constants of K and 1/n for the Freundlich isotherm in each pesticide-clay combination are listed in Table 6-2.

In general, the data obtained from these adsorption equilibrium studies revealed that the adsorptive capacities of the test clay minerals at the equilibrium state could not be correlated to their cationic or anionic exchange capacities, which are described in Chapter II (p.13); these findings are within anticipations since the mechanism of pesticide adsorption on clay mineral is not believed to be a matter of ion exchange process. Noteworthy here is the fact that the relative adsorptive capacity of the three types of clay investigated could not be generalized; instead, the adsorptive capacity was dependent upon the specific pesticide-clay combination. For example, the relative magnitude of the adsorption of DDT on different types of clay mineral decreased generally in the following order,

Montmorillonite $>$ Kaolinite $\simeq$ Illite,

and of heptachlor decreased as follows,

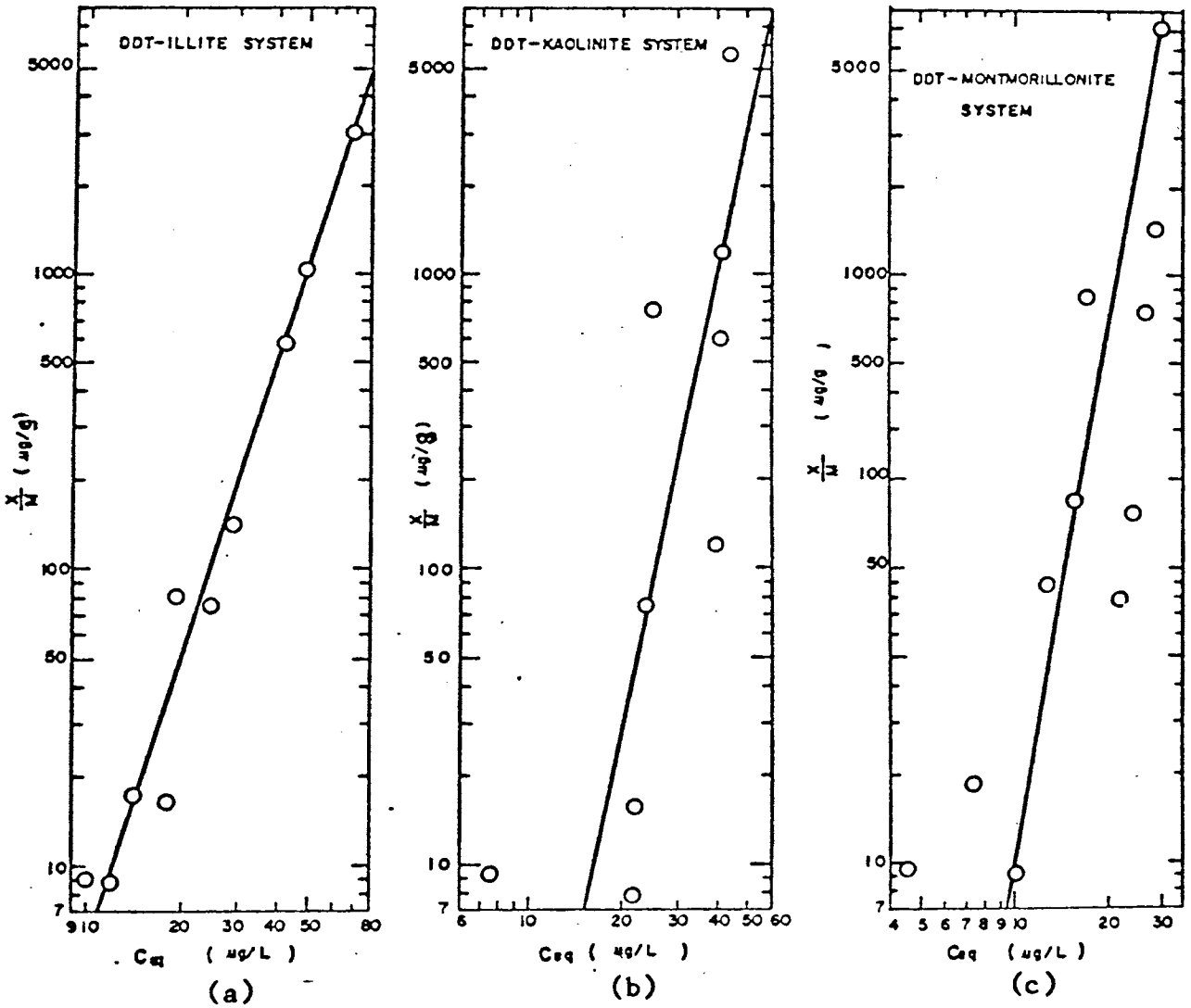


Fig. 6-1. Freundlich Adsorption Isotherm for DDT

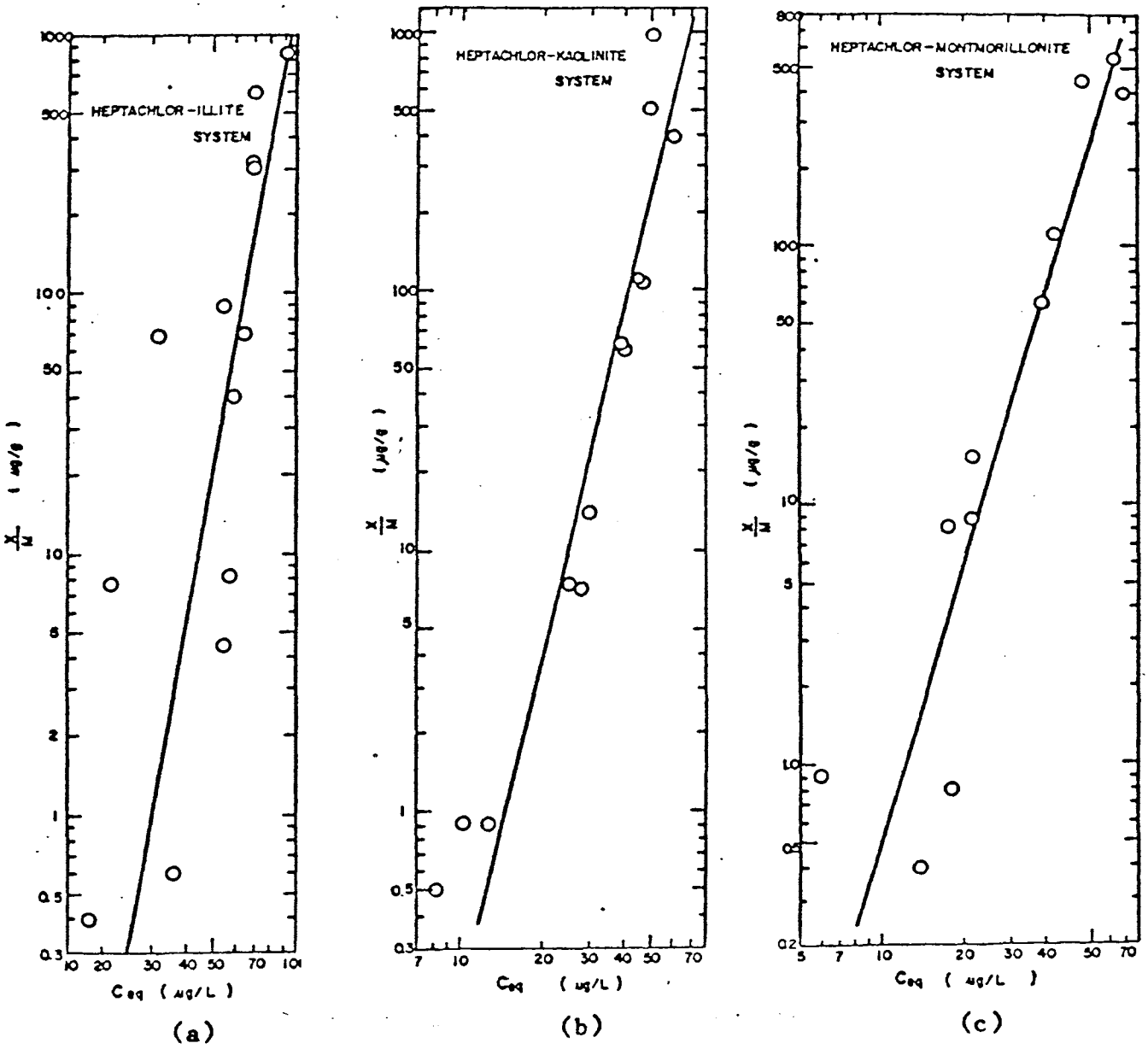


Fig. 6-2. Freundlich Adsorption Isotherm for Heptachlor

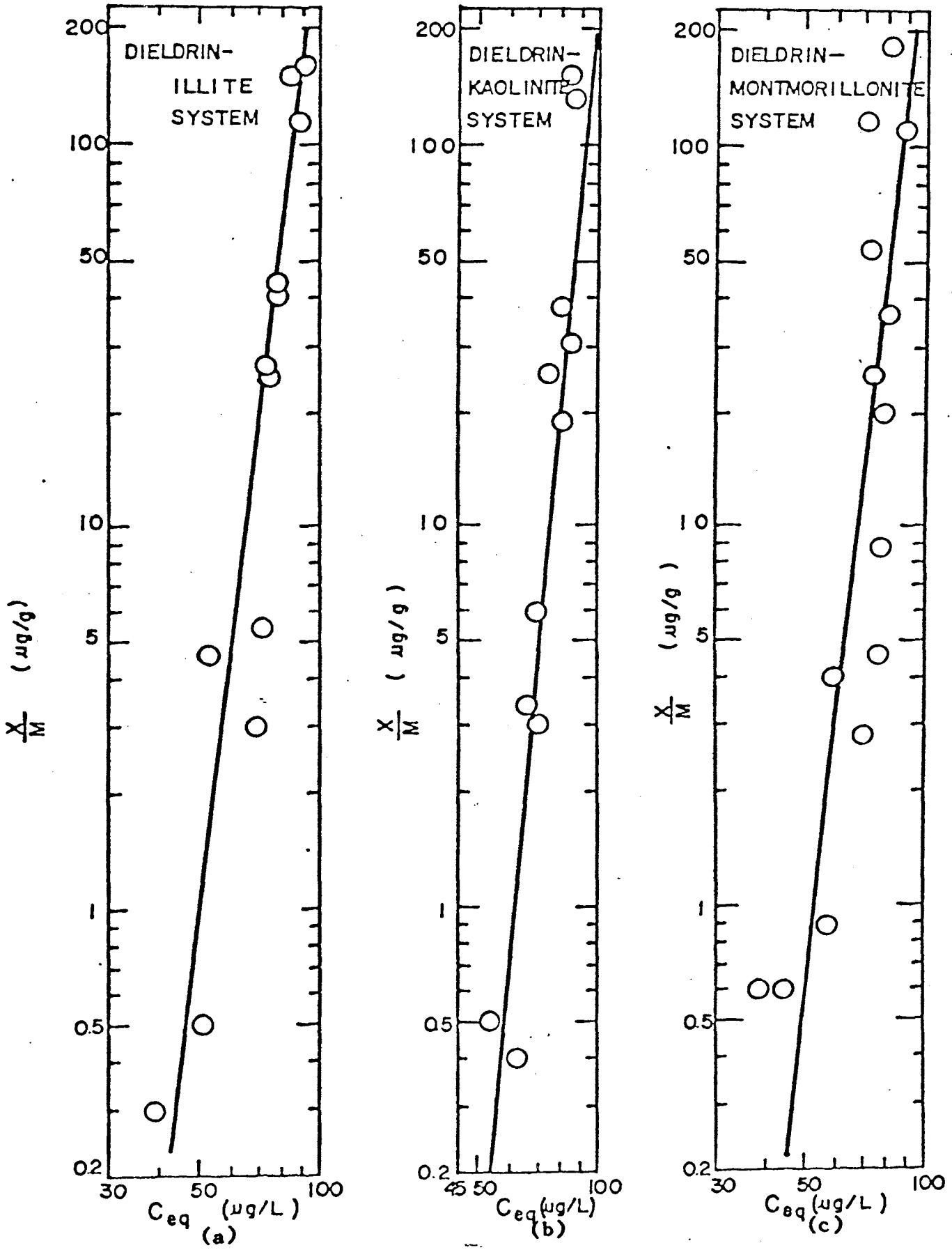


Fig. 6-3. Freundlich Adsorption Isotherm for Dieldrin

Table 6-2

Constants of Freundlich Adsorption Isotherm for

Each Pesticide-Clay Combination

Pesticide-Clay Combination	Constants of Freundlich Adsorption Isotherm	
	K	1/n
DDT-Illite	2.72×10^{-3}	3.28
DDT-Kaolinite	7.37×10^{-6}	5.08
DDT-Montmorillonite	1.10×10^{-5}	5.97
Heptachlor-Illite	1.09×10^{-9}	6.07
Heptachlor-Kaolinite	5.00×10^{-6}	4.51
Heptachlor-Montmorillonite	1.48×10^{-4}	3.52
Dieldrin-Illite	9.45×10^{-16}	8.82
Dieldrin-Kaolinite	1.46×10^{-21}	11.63
Dieldrin-Montmorillonite	1.05×10^{-16}	9.24

Montmorillonite $\simeq$ Kaolinite > Illite,

whereas the adsorption of dieldrin decreased as shown below,

Illite > Montmorillonite > Kaolinite.

The above findings suggest that the mechanism of the adsorption of pesticides on the experimental clays could involve the formation of either hydrogen bonding (a high strength binding by physical adsorption process) or some other types of chemical bond (chemical adsorption processes) between the pesticide molecules and the clay mineral structures. This suggestion could be further supported by desorption tests which were conducted in the dieldrin -montmorillonite and heptachlor-illite combined systems after the adsorption tests had been concluded. For these desorption tests, one liter of each test clay suspension was withdrawn and centrifuged for the separation of clay from liquid solution, which was next decanted and replaced with the same amount of distilled water. The new mixture was then agitated and the amount of pesticide desorbed from the clay was determined by measuring the increase of pesticide concentration in the liquid phase.

The results of the desorption tests, as shown in Table 6-3 and Fig. 6-4, indicated that the desorption of pesticide was also an instantaneous reaction, being similar to most adsorption processes as described in Chapter V. However, it was found that only very small fractions of the pesticides already adsorbed were desorbed thereafter. In the heptachlor-illite combined system the extent of desorption was so small that there was no pesticide desorption observed in the unit containing a clay concentration of 10 g/l. The following calculations may be helpful to explain how small is the extent that dieldrin was found to desorb from the montmorillonite clay:

Table 6-3

Desorption of Pesticides from Clays

Time of Reaction (hrs.)	Desorption of Pesticides (ppb)			
	Dieldrin-Montmorillonite* System Having a Clay Concentration of		Heptachlor-Illite** System Having a Clay Concentration of	
	100 g/l	10 g/l	100 g/l	10 g/l
0 (initial)	0	0	0	0
½	19.5	9.0	2.1	0
1	22.0	11.0	2.1	0
1½	17.0	9.5	2.1	0
2	17.0	13.0	4.1	0
3	15.0	15.0	3.7	0
5	7.0	7.0	3.5	0
7	10.0	9.0	3.2	0

* The initial adsorbate concentration of the adsorption test was 100 ppb; at the conclusion of the adsorption test, the equilibrium dieldrin concentrations were 39 and 61 ppb at clay concentrations of 100 and 10 g/l, respectively.

** The initial adsorbate concentration of the adsorption test was 100 ppb; at the conclusion of the adsorption test, the equilibrium heptachlor concentrations were 10 and 22 ppb at the clay concentrations of 100 and 10 g/l, respectively.

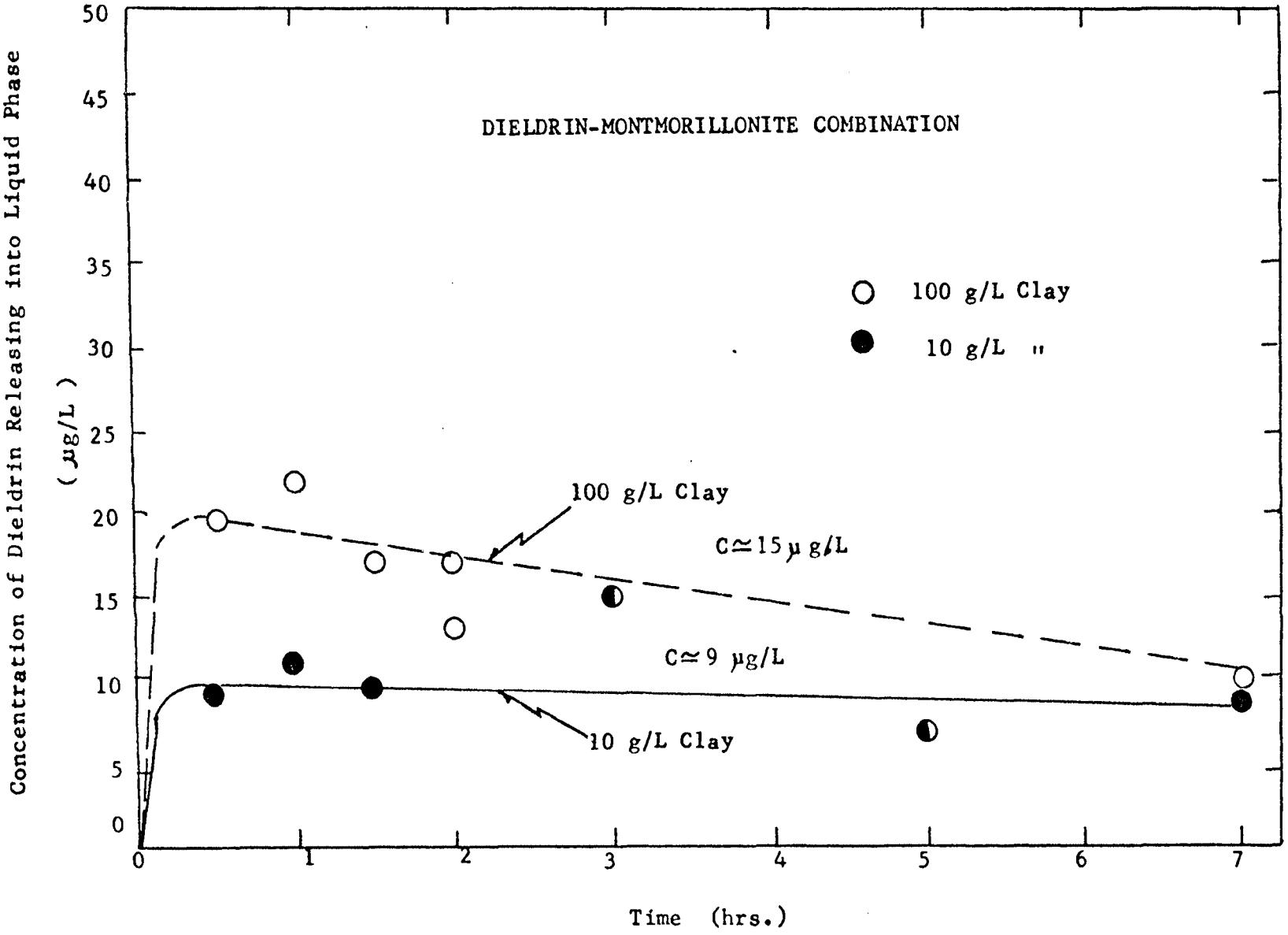


Fig. 6-4. Desorption of Dieldrin from Montmorillonite

Stage of adsorption:	1st Unit	2nd Unit
(a) Clay concentration in the suspension	100 g/l	10 g/l
(b) Initial adsorbate concentration	100 µg/l	100 µg/l
(c) Equilibrium adsorbate concentration	39 µg/l	61 µg/l
(d) Dieldrin adsorbed by clay, (b) - (c)	61 µg/l	39 µg/l
(e) Dieldrin adsorbed per gram of clay, (d) / (a)	0.61 µg/g	3.9 µg/g
Stage of desorption:		
(f) Equilibrium adsorbate concentration (from Fig. 6-4)	15 µg/l	9 µg/l
(g) Dieldrin desorbed from clay = (f)	15 µg/l	9 µg/l
(h) Dieldrin desorbed per gram of clay, (g) / (a)	0.15 µg/g	0.9 µg/g
(i) Dieldrin remaining per gram of clay, (e) _ (h)	0.46 µg/g	3.0 µg/g

Therefore, by plotting the equilibrium solute concentrations of desorption (f), i.e., C in Eq. 6-1 for Freundlich isotherm, versus the amounts of dieldrin remaining on each gram of clay (i), i.e., x/m in Eq. 6-1, on log-log paper, two data points can be obtained for the desorption isotherm of the dieldrin-montmorillonite system, as shown in Fig. 6-5. If the adsorption of dieldrin by montmorillonite was a process of physical adsorption caused by electrostatic or interparticle attractions, the two data points of the desorption isotherm as calculated above must coincide with the adsorption isotherm, shown in Fig. 6-3c; that is to say, if the amount of dieldrin remaining on clay was 0.46 µg per gram of clay, the liquid phase should have a corresponding equilibrium solute concentration of 46 µg/L to equilibrate the sorption and desorption processes. Therefore, due to the small extent of pesticide desorption observed in these tests, it may be concluded that the uptakes of chlorinated hydrocarbon pesticides by clay materials were accomplished predominantly by chemical adsorption processes, or by certain physical adsorption processes which involved the formation of certain high energy bonds such as hydrogen bonding.

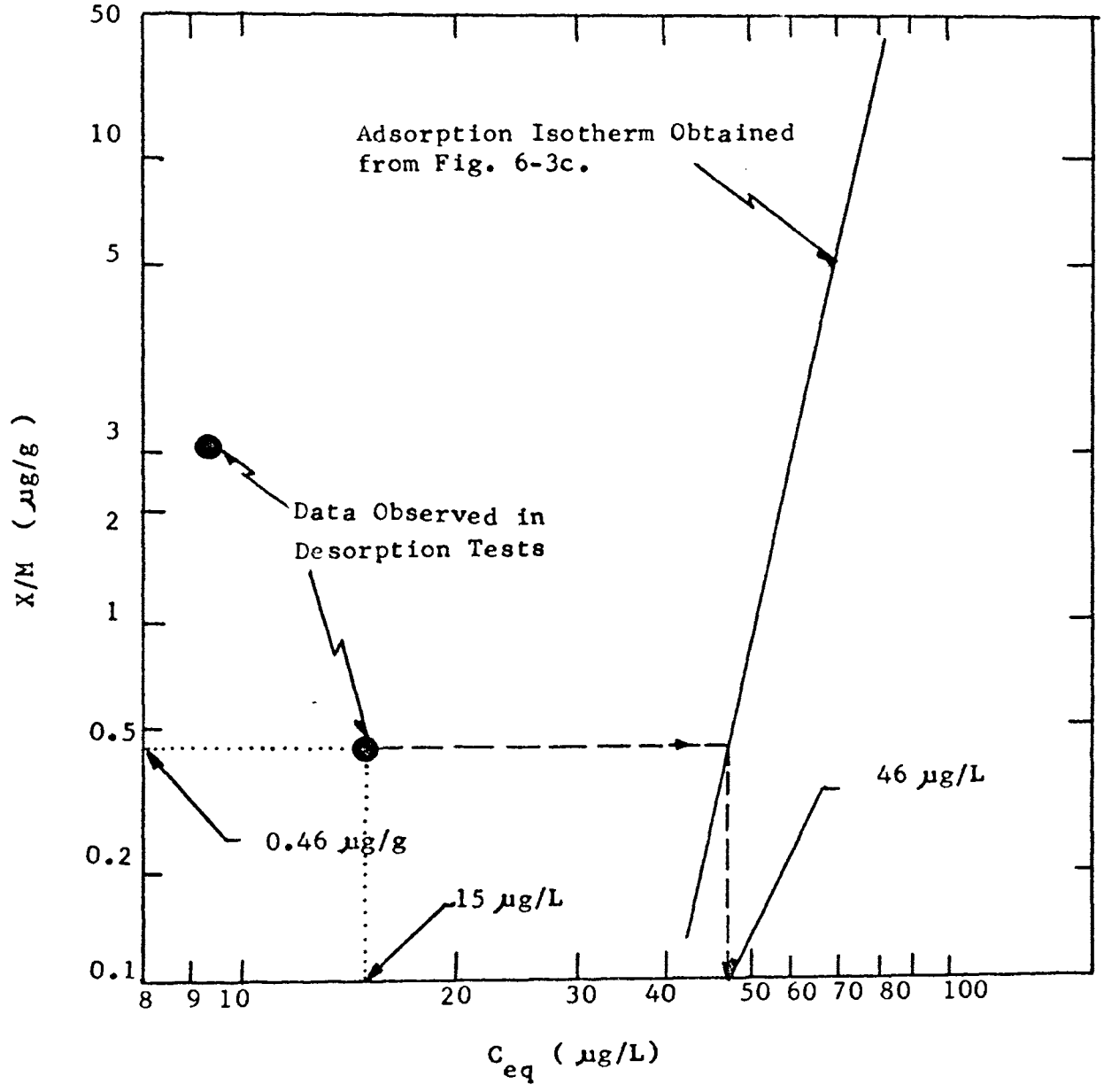


Fig. 6-5. Desorption Isotherm for Dieldrin-Montmorillonite Combination

CHAPTER VII

AQUATIC MODEL STUDIES OF SORPTION AND DESORPTION

The batch studies of adsorption, including evaluations of rates of uptakes and adsorption equilibria (see Chapters V and VI), were performed as the first step to investigate the fundamental adsorption reactions in the selected pesticide-clay systems. In order to gain a better insight into the effect of certain important environmental factors, including pH, temperature and salt (NaCl) concentration of water, on the behavior of the sorption and desorption processes, a series of aquatic model studies were conducted.

A. General Experimental Approach and Procedure

The aquatic model studies were conducted in a series of laboratory-controlled aquatic systems composed of 10-gallon glass aquaria. Each of these aquaria was separated into two equal compartments by inserting a piece of glass in the middle of the aquaria, as shown in Fig.7-1. One of the compartments in each aquarium received the test pesticide-clay suspension while the aqueous pesticide solution was added to the other to serve as a control.

Only the dieldrin-montmorillonite combination was selected for the aquatic model studies primarily because a) the volatilization of dieldrin is slow in an aqueous system, b) the efficiency for dieldrin extration from an aqueous solution is almost 100 per cent, c) montmorillonite has a large adsorption capacity for dieldrin. In addition, the adsorption of dieldrin by several types of soil has been reported in the literature (20), so that the selection of dieldrin as the test material would allow the results

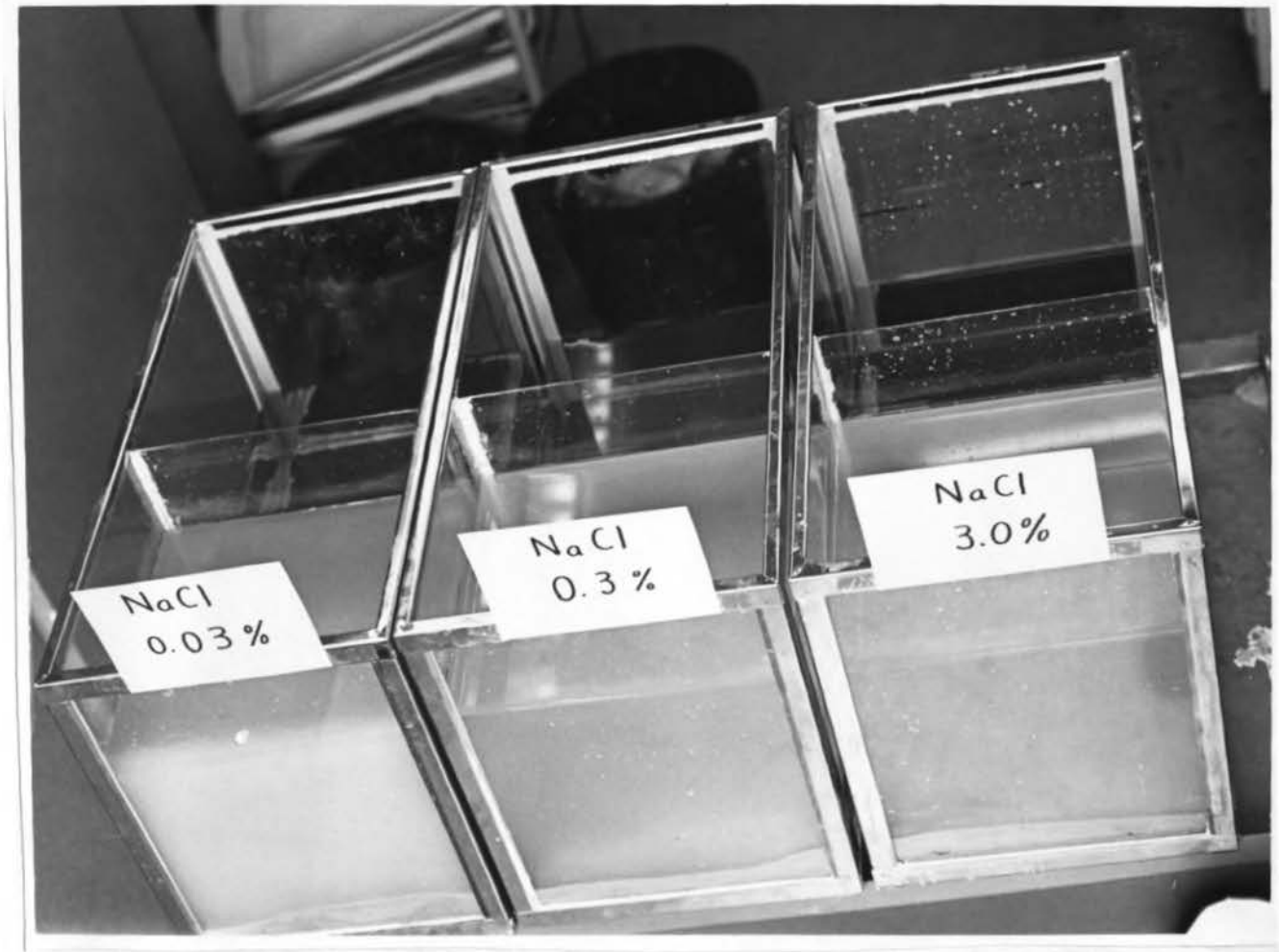


Fig. 7-1. Experimental Setup for Aquatic Model Studies

obtained from this reserch to be compared with other investigators' findings.

The environmental stresses selected for the studies included pH, temperature and salt (NaCl) concentration of water, all of which are able to exert significant effects on most physical,chemical and biological reactions. In addition, these three environmental factors can be controlled easily in the laboratory.

The effect of pH was studied at three levels, 6.0 and 10.0 which represent the extreme limits, and 8.0 which represents the average pH values observed in most natural aquatic systems. A 10^{-2} Mole of carbonate-bicarbonate solution, buffered at the proper pH as indicated above, was used for the preparation of the pesticide solutions. The proper recipes for the preparation of these buffer solutions were calculated from Henderson-Hes selbalch Equation (16). Temperature was studied at three levels, 10°C, 20°C, and 30°C, representing the average temperatures found in the cold, moderate, and hot seasons. Two walk-in incubators, heated and refrigerated, were used for the temperature controls. Salt concentration was investigated at three levels, 0.03, 0.3 and 3.0 per cent by weight, which signify the salt concentrations found in lakes, brackish waters, and bays, respectively.

In evaluating the effect of the different environmental factors, only one factor was varied in each separate series of tests while the other factors were constant. Generally, the pH was maintained at 8.0 and the temperature at 20°C; distilled water was used for the preparation of the pesticide solution.

The general test procedures for both sorption and desorption studies were as follows. In the sorption studies, a quantity of 1500 grams of the montmorillonite clay was spread uniformly over the bottom of one compartment

of each aquarium, then 15 liters of the pesticide solution was added to each of all compartments. The system was not agitated in order to simulate as close as possible to the condition existing in a lake. Each of the test aquaria was then subjected to the intended environmental control as mentioned above. The concentrations of the test pesticide remaining in the liquid phase of all compartments were determined at various time periods until an equilibrium state was reached. The gas chromatographic procedure (see Appendix I) employed in the previous studies was used for the determination of pesticides.

The desorption studies were conducted after the equilibria had been reached in the adsorption studies. The liquid in each compartment containing the test clay suspension was drained off by siphoning and then replenished with distilled water while the control compartments remained the same without any disturbance. The concentrations of the pesticide desorbed from the clay into the liquid phase in the test suspensions or remaining in the controls at various time intervals were determined by the same gas chromatographic procedure until an equilibrium state was again reached.

B. Results and Discussion

The results obtained from the aquatic model studies are tabulated in Tables 7-1, 7-2 and 7-3; these data are also plotted in Figs. 7-2, 7-3 and 7-4.

Similar to the findings reported by many other investigators (2,6,14, 20), all of the three environmental factors evaluated in these studies appeared to exert only slight or no effects on the dieldrin sorption and desorption by montmorillonite clay. For example, at the pH of 8.0 and 10.0 there was no substantial difference in the dieldrin uptakes by montmoril-

lonite, Fig. 7-2. When the pH was lowered to 6.0, which represented 100 and 10,000 folds of increase in the hydrogen ion concentration as compared to the pH of 8.0 and 10.0, respectively, the quantity of dieldrin adsorbed by montmorillonite was increased by an order of about 20 per cent, as calculated below:

	pH 6.0	pH 8.0
(a) Initial solute concentration	100 ppb	100 ppb
(b) Equilibrium solute concentration	67 ppb	73 ppb
(c) Reduction in pesticide concentration due to adsorption	33 ppb	27 ppb
(d) Per cent increase in pesticide adsorption at pH 6.0 as compared to pH 8.0	(33 - 27)/27 =	22 %

Although the hydrogen ion concentration of the liquid solution did not impart a significant effect on the adsorption reaction, a higher concentration of hydrogen ion was able to enhance the retaining of the pesticide molecules already adsorbed by clay, thus reducing the subsequent pesticide desorption, as shown in the desorption curves of Fig. 7-2. One of the possible explanations for this observation might be that a high concentration of hydrogen ion present in the solution could make the pesticide molecules loaded and positively charged with the H^+ ion, which would then coordinate with the surface OH^- of the clay mineral to form the hydrogen bondings (a relatively high energy bonding due to physical adsorption reaction).

Although temperature was found to influence the rate of pesticide volatilization in the control units, it is interesting to note that temperature did not affect the rates and quantities of the sorption and desorption of dieldrin by montmorillonite, as shown in Fig. 7-3. This, according to the Arrhenius principle for the reaction rate (6), would reflect that the activation energy of the adsorption of dieldrin by montmorillonite is relatively high, which is a further evidence to support the previous postulation (see Chapter VI, p. 90) that the adsorptions of chlori-

Table 7-1

Effect of pH on the Dieldrin Uptake by Montmorillonite

Time of Reaction	Concentration of Dieldrin Remaining (ppb)					
	pH 6.0		pH 8.0		pH 10.0	
	Clay Suspension	Control	Clay Suspension	Control	Clay Suspension	Control
Adsorption						
0 min. (initial)	100.0	100.0	100.0	100.0	100.0	100.0
2 "	63.7	100.0	67.3	100.0	71.4	100.0
30 "	74.2	-	67.6	-	75.0	-
1 hr.	70.4	99.8	74.4	105.0	74.4	105.0
1½ "	74.6	105.0	74.6	105.0	72.4	102.0
2 "	73.2	110.0	74.6	102.0	75.8	102.0
3 "	69.2	102.0	74.2	92.2	70.6	97.0
5 "	66.7	104.0	77.3	112.0	74.1	98.2
7 "	70.5	103.0	75.0	91.0	68.1	98.2
12 "	67.4	85.5	72.8	91.0	74.4	86.6
24 "	66.4	80.3	73.7	81.3	72.1	83.0
36 "	-	-	-	-	-	-
48 "	-	57.0	-	74.6	-	60.5
Desorption						
0 min. (initial)	0.0	57.0	0.0	74.6	0.0	60.5
2 "	9.9	57.0	14.7	74.6	14.2	60.5
30 "	9.6	65.0	12.2	65.7	16.5	66.0
1 hr.	7.2	51.5	16.4	70.0	16.6	79.5
1½ "	10.2	83.0	17.4	87.0	18.8	74.5
2 "	12.6	73.5	14.3	74.0	17.6	74.0
3 "	12.5	75.6	19.2	77.6	18.0	73.0
5 "	9.3	68.6	21.2	75.5	18.0	74.0
7 "	8.9	74.0	14.4	69.2	15.5	68.5
12 "	9.9	65.7	16.6	72.6	20.6	76.6
16 "	-	-	-	-	-	-
24 "	9.1	48.0	14.5	58.4	20.1	60.2

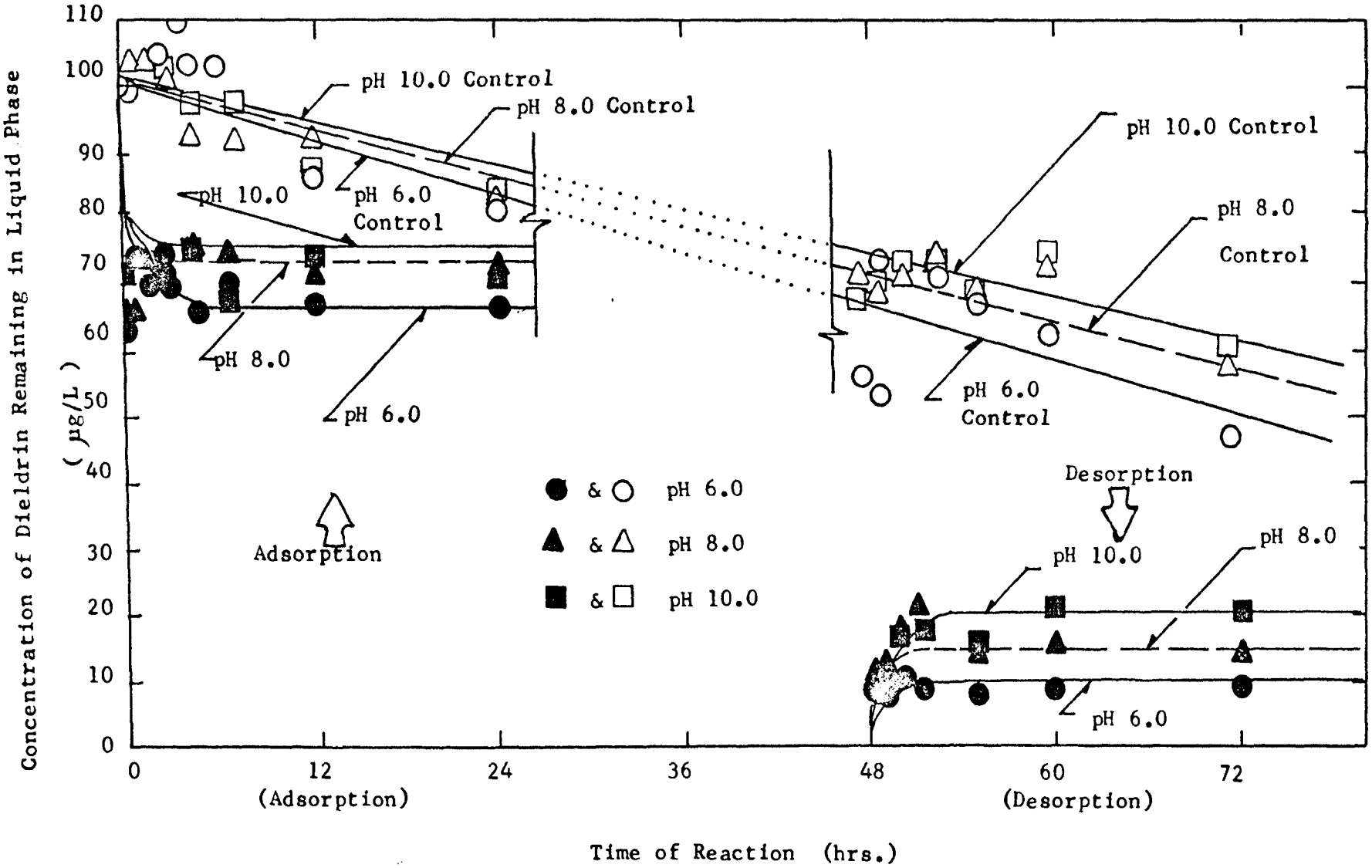


Fig. 7-2. Effect of pH on the Dieldrin Uptake by Montmorillonite

Table 7-2

Effect of Temperature on the Dieldrin Uptake by Montmorillonite

Time of Reaction	Concentration of Dieldrin Remaining (ppb)					
	10°C		20°C		30°C	
	Clay Suspension	Control	Clay Suspension	Control	Clay Suspension	Control
Adsorption						
0 min. (initial)	100.0	100.0	100.0	100.0	100.0	100.0
2 "	70.0	100.0	80.0	100.0	70.6	100.0
30 "	59.0	98.5	72.0	95.5	54.0	96.0
1 hr.	63.0	87.0	61.8	98.0	52.2	92.0
1½ "	65.0	93.0	67.0	97.5	75.0	99.0
2 "	65.2	99.7	77.0	99.4	73.5	96.0
3 "	65.0	94.8	78.0	102.4	63.6	95.3
5 "	64.1	94.5	77.0	98.5	63.4	95.5
7 "	66.8	93.2	63.5	95.6	64.7	98.8
12 "	63.0	83.5	70.0	93.0	68.0	82.5
24 "	58.0	78.5	66.6	87.0	60.0	67.7
36 "	-	-	-	-	-	-
48 "	-	48.6	-	64.0	-	56.2
Desorption						
0 min. (initial)	0.0	48.6	0.0	64.0	0.0	56.2
2 "	11.7	48.6	8.7	64.0	11.8	56.2
30 "	9.7	48.0	10.0	68.4	10.0	50.0
1 hr.	13.4	45.0	9.6	59.0	6.8	51.4
1½ "	8.6	48.2	6.4	63.0	12.5	51.0
2 "	12.4	47.7	12.7	64.0	14.7	48.6
3 "	13.0	48.0	10.4	63.2	9.1	46.2
5 "	13.8	42.0	11.1	68.0	9.5	40.6
7 "	9.1	40.6	12.5	68.0	9.1	36.6
12 "	12.6	39.2	9.8	63.5	11.2	36.0
16 "	-	-	-	-	-	-
24 "	13.1	37.4	11.5	55.6	11.2	33.8

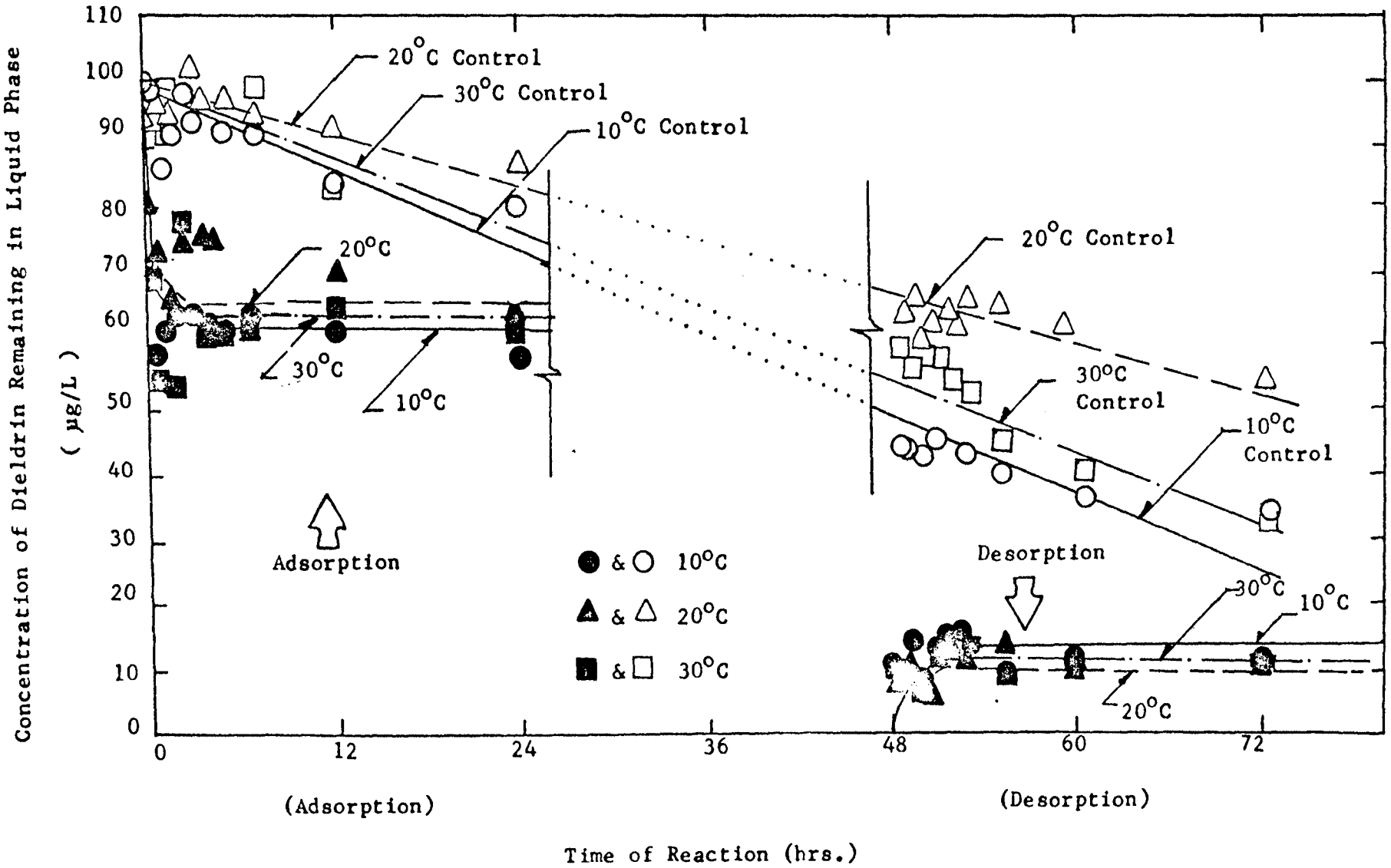


Fig. 7-3. Effect of Temperature on the Dieldrin Uptake by Montmorillonite

Table 7-3

Effect of Salt Concentration on the Dieldrin Uptake by Montmorillonite

Time of Reaction	Concentration of Dieldrin Remaining (ppb)					
	0.03% NaCl		0.3% NaCl		3.0% NaCl	
	Clay Suspension	Control	Clay Suspension	Control	Clay Suspension	Control
Adsorption						
0 min. (initial)	100.0	100.0	100.0	100.0	100.0	100.0
2 "	72.5	100.0	74.4	100.0	70.0	101.0
30 "	74.2	102.0	76.5	102.0	70.0	101.0
1 hr.	78.3	107.0	82.3	106.0	75.0	103.0
1½ "	69.6	106.0	85.2	101.0	65.6	100.0
2 "	75.7	90.7	79.0	100.0	67.5	92.0
3 "	75.6	101.0	82.3	107.0	78.0	101.0
5 "	79.3	101.0	80.1	102.0	72.0	103.0
7 "	81.0	99.0	83.5	97.0	67.5	101.0
12 "	75.0	93.0	81.5	106.0	69.5	91.0
24 "	70.3	80.0	76.5	88.0	60.5	82.5
36 "	67.0	82.5	71.0	83.5	55.7	75.0
48 "	-	73.0	-	77.0	-	63.3
Desorption						
0 min. (initial)	0.0	73.0	0.0	77.0	0.0	63.3
2 "	14.8	73.0	18.1	77.0	15.2	63.3
30 "	16.7	67.5	17.5	74.2	12.1	67.7
1 hr.	15.0	66.8	18.0	72.6	12.6	60.5
1½ "	15.7	60.5	16.6	69.2	14.0	68.5
2 "	15.6	64.5	17.5	69.5	13.0	67.4
3 "	16.0	68.0	17.5	67.5	11.3	67.0
5 "	14.1	65.0	18.5	65.0	13.9	64.5
7 "	14.6	64.7	15.7	64.0	13.9	63.0
12 "	14.4	64.5	16.8	64.2	13.0	58.7
16 "	14.0	63.5	17.7	60.6	12.1	56.1
24 "	13.0	62.0	15.7	58.5	11.3	53.0

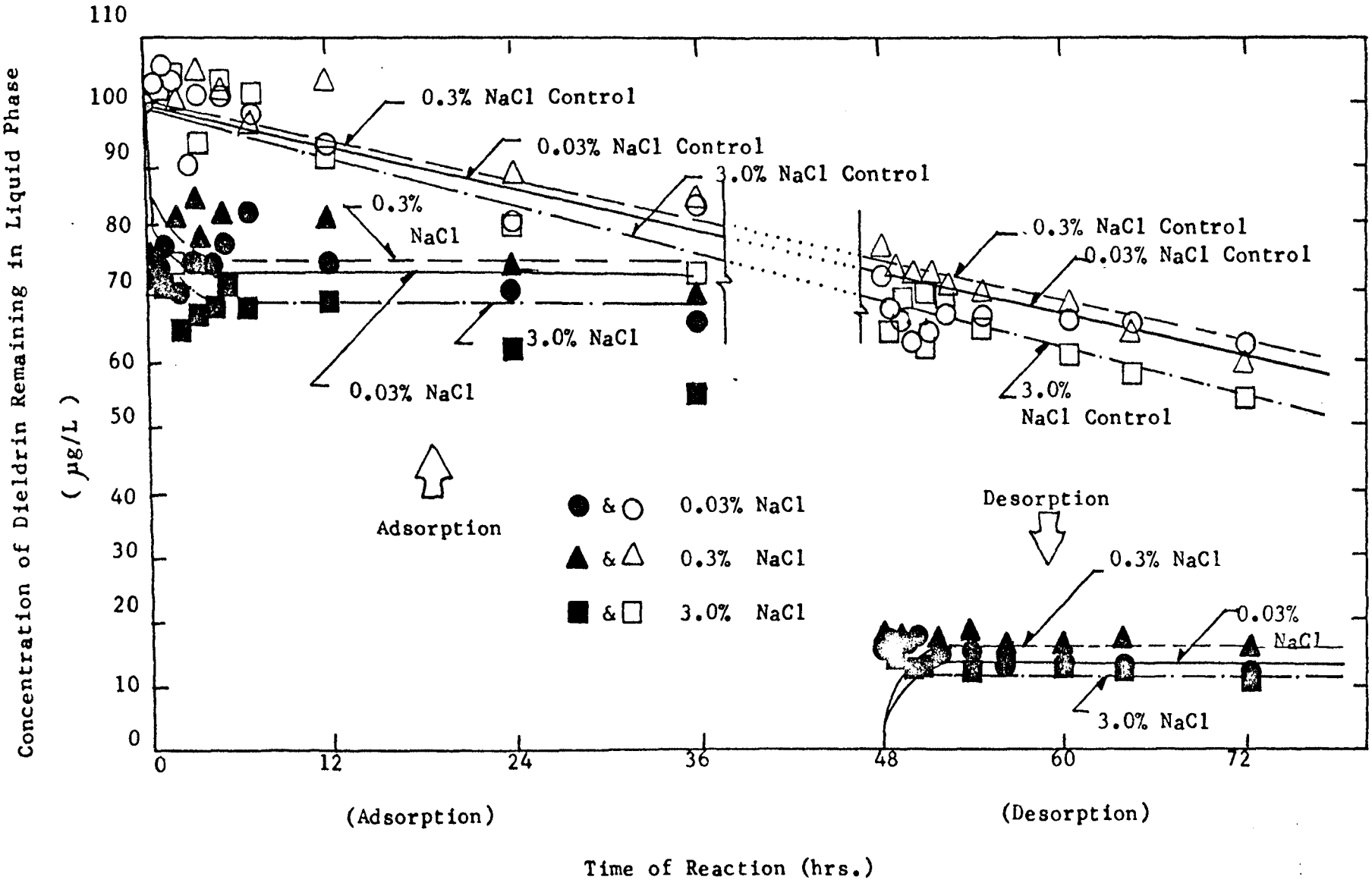


Fig. 7-4. Effect of Salt Concentration on the Dieldrin Uptake by Montmorillonite

nated hydrocarbon pesticides by the experimental clays may involve the formation of certain high energy bonds between the pesticides and the clay minerals.

The effect of salt concentration on the sorption and desorption of dieldrin by montmorillonite clay could not be generalized. As shown in Fig. 7-4, more dieldrin was adsorbed and retained stronger on clay at a high salt concentration of 3 per cent than at low concentrations of 0.3 and 0.03 per cent. However, the clay in the lower salt concentration of 0.03 per cent was found to adsorb more and retain stronger the pesticide than in the higher salt concentration of 0.3 per cent. No good explanations can be given at this time for this finding.

Finally it must be pointed out that the clay concentration used in these aquatic model studies was set at 100 g/l in all tests, and the final equilibrium concentrations of dieldrin observed in the test suspensions were found to be between 65 and 85 ppb, with an average of about 70 ppb. In the previous studies of rates and equilibria of uptakes, it was found that the equilibrium solute concentration in the dieldrin-montmorillonite system having a clay concentration of 100 g/l was approximately 40 ppb (see Fig. 5-2, p. 64). Therefore, the adsorptive capacity of montmorillonite for dieldrin in the aquatic model system was only about 50 per cent (i. e., $(100 - 70)/(100 - 40) = .50$) of that observed in the batch test unit. The discrepancy of these data obtained from the aquatic model studies and the batch studies was primarily due to the fact that the former were conducted under an agitation-free condition in the test clay suspension while the latter were conducted under completely mixed conditions.

CHAPTER VIII

DISCUSSION

In recent years, there have been many investigations concerned with the behavior of organic pesticides in soils. Most of these studies have oriented toward the determination of the efficiencies of pesticides for pest controls under a wide variety of field applications and conditions. For instance, field surveys of the residual pesticidal activities for different types of chemicals in various soil conditions have been the common subject for many studies.

A significant amount of work has also been done on the evaluation of the toxicities of pesticides to various types of organisms. These studies have disclosed that most organic pesticides are extremely toxic, not only to agricultural pests, but also to birds, animals, aquatic organisms and humans. Trace amounts of pesticides can be physiologically concentrated in animal tissues to sufficient levels to kill the animal. Findings of these toxicity studies have caused great public concern about the widespread contamination of pesticides in the environment, and also generated great research interests in the determination of the fate of these organics after their applications in the field. However, most of the studies have been limited to the field work of survey type such as monitoring the concentration of pesticides in soils, crops and agricultural runoffs following each application of these chemicals. Only a few investigators have conducted studies in the interest of water quality management and pollution control to gain a better insight into the behavior of sorption and desorption of organic pesticides by soils and clays.

Among the limited number of studies dealing with the adsorption of pesticides by soils, clays or aquatic sediments, there have been some contradictory findings regarding the extent of influence that certain factors may exert upon the adsorption reaction. For example, Eye (20) found that the adsorption of dieldrin by a soil sample was not dependent upon the clay content or the specific surface area of the soil, while Chesters (14) observed that the adsorption of lindane by aquatic sediments was related to the clay content and the particle size of the sediments. Therefore, it was deemed necessary that further basic research studies must be undertaken to evaluate the fundamental adsorptions of organic pesticides by soils and clays, and also ascertain the effects of important environmental factors upon the adsorption reactions.

The research study described in this thesis fills that need. Results obtained from this study indicated that chlorinated hydrocarbon insecticides were adsorbed easily by clay minerals. In general, the adsorptions of these organochlorine pesticides by clays were almost instantaneous reactions; in many cases the adsorption equilibria were reached within a period of less than two hours (see Chapter V). The unusually rapid uptakes of chlorinated hydrocarbon pesticides by clay minerals may be due to the following:

(a) Chlorinated hydrocarbon pesticides are extremely hydrophobic in nature so that they have strong tendencies to concentrate on the liquid-solid interface such as the clay particle surface.

(b) Pesticide molecules may have certain functional groups or polar ends which can react or coordinate with the corresponding groups of the clay minerals, thereby forming some types of high strength bonding.

Between the two prior reasons, it is believed that the latter is much more significant than the former in controlling the process of the adsorption

of pesticide by clay mineral. Otherwise, the extent of adsorption would seem to be largely dependent upon the pesticide solubility and the specific surface area of the clay particle. It was found that in this study the relative adsorptive capacities of the three types of clay investigated could not be generalized (see Chapter VI); instead, the adsorptive capacity of each clay was dependent upon the specific pesticide-clay combination.

The small extent of pesticide desorptions as reflected by the non-coincidence of the sorption and desorption isotherms (see Chapter VI, p. 82), and the relative independence of the adsorption and desorption reactions to the variation of temperature (see Chapter VII, p.95) are other evidences suggesting that the uptake of chlorinated hydrocarbon pesticides by clay minerals is a process of chemical adsorption, which involves the formation of certain types of high energy bonding. The application of the infrared spectroscopy for the actual identification of the bondings formed on clay surface may be a proper way for the final proof of the above postulation.

Since clay minerals were found to have high adsorption capacities as well as strong retaining potentials for chlorinated hydrocarbon pesticides, it seems practical to use these clays as the pesticide carriers in the future agricultural application of these chemicals in order to reduce the amount of pesticides transported into the natural water bodies through agricultural runoffs. However, before this practice can be permitted additional research studies must be carried out to determine if there is any reduction in the residual pesticidal activity for the pesticide already adsorbed on clay.

It should be pointed out that many investigators have reported that the presence of organic matter in a soil tends to promote a long-life

retaining of pesticide residues in the soil (14,20,34). Although most of these investigators were concerned with the residual insecticidal activity rather than the water pollution potential, their findings would indicate that organic pollutions may be able to play an important role in controlling the pesticide sorption and desorption reactions. Unfortunately, in order to maintain the relatively simple experimental systems in this study, the effects of organic matter on the sorption and desorption of pesticides by clays were not evaluated. Further research work remains to be done in this area.

CHAPTER IX

CONCLUSIONS

On the basis of the findings obtained from this investigation, the following conclusions were drawn:

1. All the three chlorinated hydrocarbon pesticides evaluated in this study, i.e., DDT, dieldrin and heptachlor, were easily adsorbed by the clay minerals of illite, kaolinite and montmorillonite. DDT appeared to be adsorbed in the largest quantity, heptachlor was next and dieldrin adsorbed the least.

2. The adsorptions of the chlorinated hycrodarbon pesticides on illite and kaolinite were nearly instantaneous reactions with the adsorption equilibria being reached within one hour of the reactions. However, the adsorptions of these pesticides on montmorillonite appeared to be a gradual progression and the reactions could be divided into the following three distinct stages: the instantaneous adsorption stage, the gradual adsorption stage caused by the diffusion of the pesticide molecules into the clay interlamellar spacings, and the final equilibrium stage.

3. The equilibrium adsorptions of the tested pesticides on the experimental clay minerals were in reasonable accord with the Freundlich adsorption isotherm. However, the relative adsorption capacities of the clay minerals were not correlated to their ion exchange capacities.

4. The relative adsorption capacities of the experimental clays for DDT decreased in the following order,

$$\text{Montmorillonite} > \text{Kaolinite} \simeq \text{Illite},$$

and for heptachlor decreased as follow,

$$\text{Montmorillonite} \simeq \text{Kaolinite} > \text{Illite},$$

whereas the adsorptions for dieldrin decreased as shown below,

Illite > Montmorillonite > Kaolinite

5. Only very small fractions of the chlorinated hydrocarbon pesticides already adsorbed by clay minerals were desorbed thereafter; yet, the desorption reactions occurred instantaneously.

6. The hydrogen ion concentration of water did not appear to exert significant effects on the montmorillonite adsorption for dieldrin. However, a decreasing pH was able to enhance the retaining of the pesticide already adsorbed by the clay, thereby reducing the subsequent pesticide desorption.

7. Temperature did not materially affect the rate and the quantity of the sorption and desorption of dieldrin by montmorillonite.

8. The effect of the salt (NaCl) concentration of water on the dieldrin sorption and desorption by montmorillonite could not be generalized. The relative extents of the dieldrin sorption and desorption were found to be the largest in the 3 per cent salt solution, next in the 0.03 per cent, and the smallest in the 0.3 per cent salt solution.

9. The mechanism of the adsorptions of the chlorinated hydrocarbon pesticides by the experimental clay minerals could have involved the formation of the hydrogen bonding or some other types of high strength chemical bonds between the pesticide molecules and the clay mineral structures.

10. Since clay minerals have high adsorption capacities and strong retaining potentials for chlorinated hydrocarbon pesticides, these clays may be used as the pesticide carriers in the future agricultural applications of these chemicals in order to reduce the pesticide polution of natural waters through the agricultural runoffs.

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APPENDICES

APPENDIX I

GAS CHROMATOGRAPHIC ANALYSIS OF CHLORINATED HYDROCARBON PESTICIDES

The aqueous solubilities of chlorinated hydrocarbon pesticides such as DDT, dieldrin and heptachlor are on the order of parts per billion (ppb). Trace quantities of these pesticides present in water can not be accurately measured without the use of some sophisticated instrument such as the gas matograph employing an electron capture detector. For this research determinations were made with a Varian Aerograph Gas Chromatograph, Model 1520-1B (see Chapter III, p.25).

The electron capture detector is tremendously sensitive to chlorinated compounds and therefore, able to analyze a pesticide concentration in the ppb range (32). It is also conveniently not sensitive to ordinary volatile organic compounds which are invariably present in extracts of plant material. Thus, troublesome and messy clean-up procedures are largely avoided. However, this type of detector will become non-functionable if trace amounts of water vapor pass through the detector cell. As a consequence, direct injection of aqueous pesticide solution into the gas chromatograph is not permitted. The pesticide in aqueous solution must be first extracted with a selected solvent such as hexane and the extract is then subjected to the gas chromatographic analysis. The following paragraphs will describe the procedures employed in this study for the pesticide extraction and the gas chromatograph operation.

A. Pesticide Extraction Procedure

1. Pipet 25.0 ml of the test clay suspension into a 50-ml size Pyrex glass centrifuge tube.

2. Centrifuge the clay suspension for 5 min. to separate solids from liquid solution.

3. Pipet 20.0 ml of the supernatant into a separatory funnel.

4. Add 4.0 ml of hexane to the separatory funnel.

5. Shake manually the separatory funnel for 2 min., then allow it to stand for about 5 min. in order to separate hexane from the liquid solution.

6. Drain off the liquid solution first and then collect the hexane extract in a 10-ml test tube.

7. Cap the test tube and keep it in the refrigerator until the extract is ready for injection into the gas chromatograph. (Note: The hexane extract should not be stored more than 24 hours before the injection in order to minimize the loss of pesticide.)

B. Gas Chromatograph Operation Procedure

1. Set up the following accessories on the gas chromatograph for the analysis of chlorinated hydrocarbon pesticides:

   a. Pyrex glass injector tube
   b. Pyrex glass column packed with 5 % Dow-11 on 80/100 mesh high performance chromosorb W
   c. Electron capture detector
   d. High purity nitrogen gas

   (Note: all these accessories except the nitrogen gas are products of Varian Aerograph)

2. Adjust the gas chromatograph to the following operation conditions at least 30 min. prior to the injection of samples.

   a. column temperature 180°C
   b. detector temperature 200°C
   c. injection temperature 200°C
   d. carrier gas flow rate N_2 at 40 ml/min.

3. Switch on the detector cell potential.

4. Switch on the recorder.

5. Use the attenuation and bucking controls to adjust the base line of the detector signal out-put to about 90 per cent transmittance position on the recorder chart paper.

6. Use a 10-ml size Hamilton microsyringe to inject 2 µl of the hexane extract into the gas chromatograph; wait for the peak (or peaks) to appear on the chart paper before the injection of the next sample.

APPENDIX II

DETERMINATION OF ORGANIC CONTENT OF CLAY BY WET COMBUSTION TOTAL CARBON TEST*

The wet-combustion analysis of soils by chromic acid digestion has long been a standard method for determining total- and/or organic-carbon, giving results in good agreement with dry combustion. The main advantages for wet combustion are that the cost of apparatus is but a small fraction of the cost for dry-combustion equipment, and that the parts needed to assemble the apparatus are standard equipment in most laboratories.

A. Principles of Wet Combustion

The soil sample is digested in a 60:40 mixture of H_2SO_4 and H_3PO_4 containing $K_2Cr_2O_7$. The boiling temperature of this mixture, 210°C, is high enough to ensure complete oxidation of carbonaceous matter, yet low enough to prevent excessive fuming in the condenser. The CO_2 evolved is absorbed by a suitable absorbent and weighed.

The interference of Cl^-, which after digestion will form CrO_2Cl_2 and Cl_2, is prevented by using two purifying traps, one containing KI and the other containing Ag_2SO_4. Suitable materials for CO_2 absorbent are Mikhobite (G. F. Smith Chemical Co.), Caroxite or Indicarb (Fisher Chemical Co.), or Ascarite (A. H. Thomas).

B. Method of Wet Combustion

1. Apparatus: The apparatus, as shown in Fig. A2-1, for the wet combustion are assembled from the following parts**:

---

* See Reference (1).

** The capital letters designated for the parts refer to those shown in Fig. A2-1.

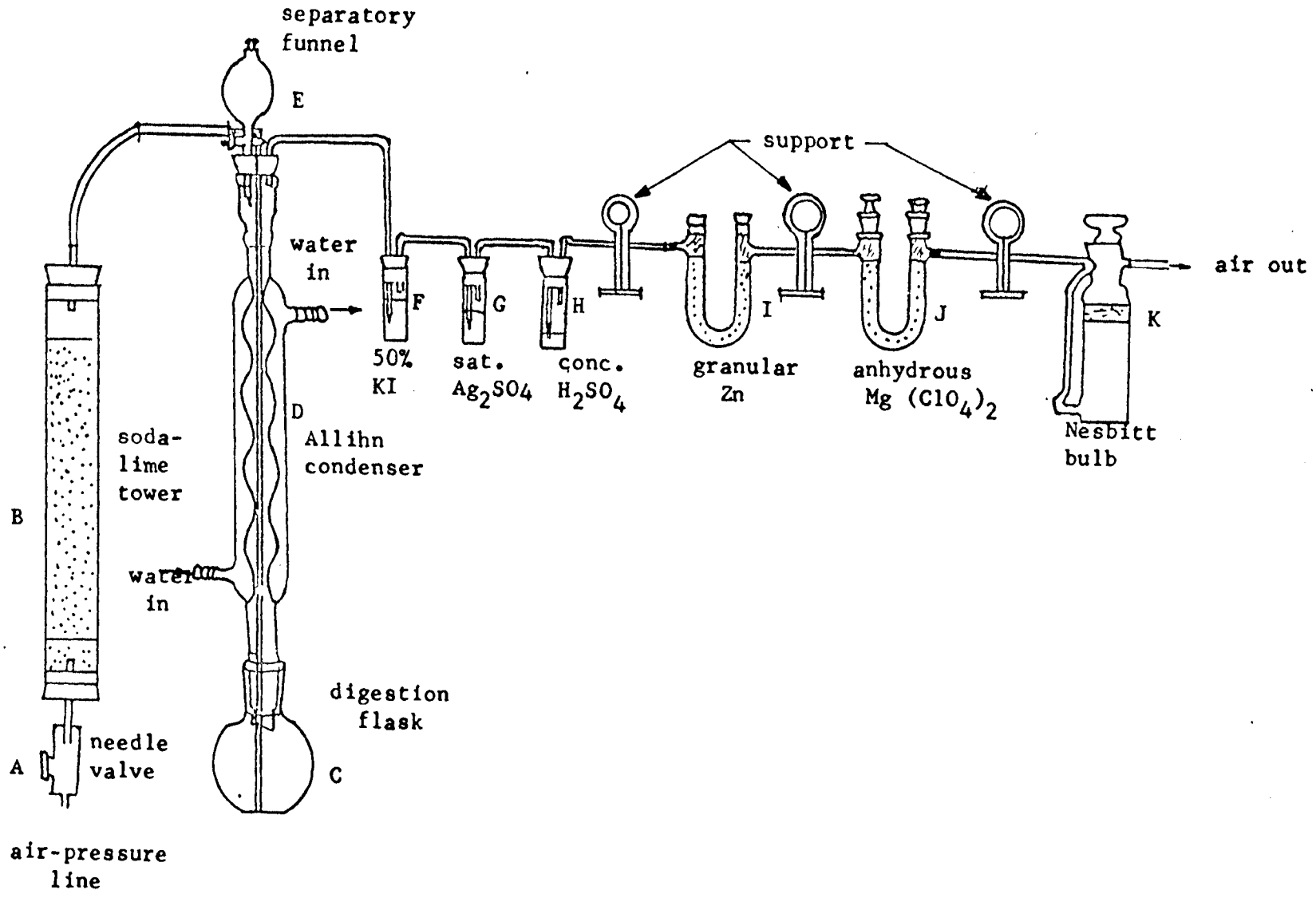

Fig. A2-1. Apparatus for the Determination of Carbon

(After Allison (1))

(A) hoke needle value
(B) soda-line tower, 10 inches high
(C) Kjeldahl flasks of 100-ml capacity to fit a No. 2 stopper
(D) Allihn 4-bulb condenser fitted with a No. 2 stopper at the delivery end
(E) open-top separatory funnel of 60-ml capacity
(F,G&H) three shell vials, 25 by 90 mm, with No, 4 stoppers
(I&J) two $CaCl_2$ U-tube, 15 cm long
(K) Nesbitt absorption bulb.

All connections of the parts are made with Neoprene stoppers and gumrubber tubing. Coat all rubber tube connections lightly with silicone lubricant.

During each test, provide a CO_2-free carrier stream by releasing air from an air-pressure line through valve A and passing it through soda-lime tower B. Connect B to a glass tube 4 mm in outside diameter that extends downward through condenser D and dips about 1 cm below the surface of the oxidizing acid in digestion flask C. Shorten the stem of funnel E to a length of about 3½ inches, and reduce the tip opening of the stem to a diameter of about 2 mm. Adjust the position of the funnel E to extend into D at least 2 inches below the stopper to avoid contact between oxidizing acid and stopper. Lubricate stopcock E with the digestion-acid mixture, or with syrupy H_3PO_4--never with regular stopcock lubricant.

Assemble the purifying traps, F to J, inclusive, on a panel 7½ inches high by 14 inches long, with attached base as shown in Fig. A2-1. Fit the vials of traps F, G, and H with No. 4 stoppers that have approximately ¼ inch of the bottom cut off to provide a tight seal with the vials. Reduce the tip openings of the inflow tubes in F and G, but not smaller than 1 mm in diameter, or sealing may occur. Fill traps F and G approximately two-thirds full with 50 per cent KI solution and saturated Ag_2SO_4, respectively. Adjust the inflow tubes so that they extend into the solutions not more than 1½ inches for trap F and ½ inch for trap G; otherwise, back-pressure may develop and cause leaks in the system.

Fill trap H not more than one-third full with concentrated H_2SO_4. Prepare the inflow tube for H from the barrel of a 5-ml pipette with tip extending not more than ½ inch into the acid (note that trap H connects directly to trap I). Place a fiber-glass disc in the bottom of the U-tube; and fill the left side, trap I, with 30-mesh granular Zn for absorbing any acid fumes that escape past H. Fill the right side, trap J, with anhydrous $Mg(ClO_4)_2$, which absorbs water from the carrier stream containing evolved CO_2 before it enters K.

Fill the Nesbitt absorption bulb K with any good, self-indicating absorbent having a high capacity for absorbing CO_2. Indicarb and Mikhobite are excellent for this purpose. When filled as shown in Fig. A2-1, the bulb contains successively a 3-cm layer of 8- to 14-mesh absorbent, a 2-cm layer of 14- to 20-mesh absorbent, and a 1-cm overlayer of anhydrous $Mg(ClO_4)_2$, with a wad of glass wool above and below the column.

2. Reagents:

   a. Digestion-acid mixture; Pour 600 ml of concentrated H_2SO_4 into 400 ml of 85 per cent H_3PO_4, cool the mixture, and store it in a glass-stoppered bottle. Keep the bottle well stoppered to prevent absorption of water vapor.

   b. Potassium dichromate ($K_2Cr_2O_7$), reagent grade.

   c. Potassium iodide (KI) solution, saturated.

   d. Silver sulfate (Ag_2SO_4) solution, saturated.

   e. Carbon dixide absorbent, self-indicating, 7 to 14 and 14 to 20 mesh. Suitable materials are Mikhobite (G. F. Smith Chemical Co.), Caroxite or Indicarb (Fisher Chemical Co.), or Ascarite (A. H. Thomas).

   f. Soda-lime, 8 to 14 mesh.

   g. Granular zinc (Zn), 30 mesh.

   h. Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) (Anhydrone, Dehydrite, or equivalent).

3. Procedure:

a. Place a finely ground soil or clay sample containing 20 to 40 mg of carbon (usually about 0.5 to 3.0 grams of oven-dry soil sample) into digestion flask C, and add about 1 gram of $K_2Cr_2O_7$.

b. Wash down the neck of the flask with 3 ml of distilled water, and connect the flask to condenser D.

c. Weigh the Nesbitt bulb K; attach it to the system and immediately open the valve at the top of the bulb.

d. Pour 25 ml of the digestion-acid mixture into funnel E above the condenser, and cover the funnel with a small beaker.

e. Open stopcock E, allow the acid to flow through D into flask C, and close the stopcock immediately to prevent loss of CO_2.

f. Adjust the air-delivery tube that passes through D into C so that its tip extends not more than 1 cm into the acid during digestion.

g. Turn on the cooling water.

h. Adjust the carrier stream to a flow rate of about 2 bubbles per sec., and maintain this rate during digestion.

i. Apply a flame of 5 to 6 cm high and bring the sample to boiling in 3 or 4 min. (If Cl^- is high, heat the mixture slowly at first and bring it to boiling in about 5 min.)

j. Continue gentle boiling, avoiding excessive frothing, for a total heating period of 10 min. (Reduce the rate of heating if visible white fumes of SO_3 occur above the second bulb of D during digestion.)

k. Remove the flame at the end of the digestion period, and aerate the system for 10 min. at the rate of 6 to 8 bubbles per sec.

l. Shut off the air stream and disconnect the digestion flask from the condenser when aeration is completed.

m. Close the stopcock on the Nesbitt bulb and disconnect it from the system. Brush the bulb with a camel's hair brush to remove any lint and dust, and weigh it immediately.

n. Make a blank determination using the identical procedure, but without sample. (Add 4 to 5 glass beads to the blank to prevent bumping.)

o. Calculate the total carbon content according to the following of formula:

$$\text{Total-carbon, } \% = \frac{\text{Grams } CO_2 \text{ of sample - grams } CO_2 \text{ of blank}}{\text{Grams of Water-free soil}} \times 0.2727 \times 100$$

APPENDIX III

RESULTS OF THE UPTAKE RATE STUDIES--FIRST EXPERIMENTAL RUN

Presented in this appendix are the results obtained from the first experimental run of the uptake rate studies (see Chapter V). The data are tabulated in Tables A3-1 through A3-6, and plotted correspondingly in Figs. A3-1 through A3-6.

Table A3-1. Rate of Adsorption of Heptachlor on Illite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	10	8.4	11	8.0	-	6.9	23	6.9	38	6.6
5 min.	18	8.5	25	8.1	41	6.9	42	6.7	54	6.5
10 min.	18	8.6	28	7.8	44	7.0	35	6.8	45	6.6
20 min.	13	8.5	28	7.9	57	7.0	57	7.1	57	6.8
30 min.	17	8.5	28	7.9	55	7.1	42	7.0	50	6.8
45 min.	18	8.6	32	7.8	63	7.1	52	7.1	67	6.9
1 hr.	18	8.4	35	7.8	60	7.2	43	7.1	62	6.9
1½ hr.	17	8.5	44	8.0	57	7.5	52	7.2	62	6.8
2 hr.	22	8.7	48	7.9	50	7.4	45	7.3	77	6.8
3 hr.	17	8.4	47	7.9	45	7.1	42	7.0	74	6.9
5 hr.	15	8.3	47	8.1	55	7.4	60	7.1	80	6.9
7 hr.	12	8.4	47	8.0	50	7.2	67	7.0	80	6.9

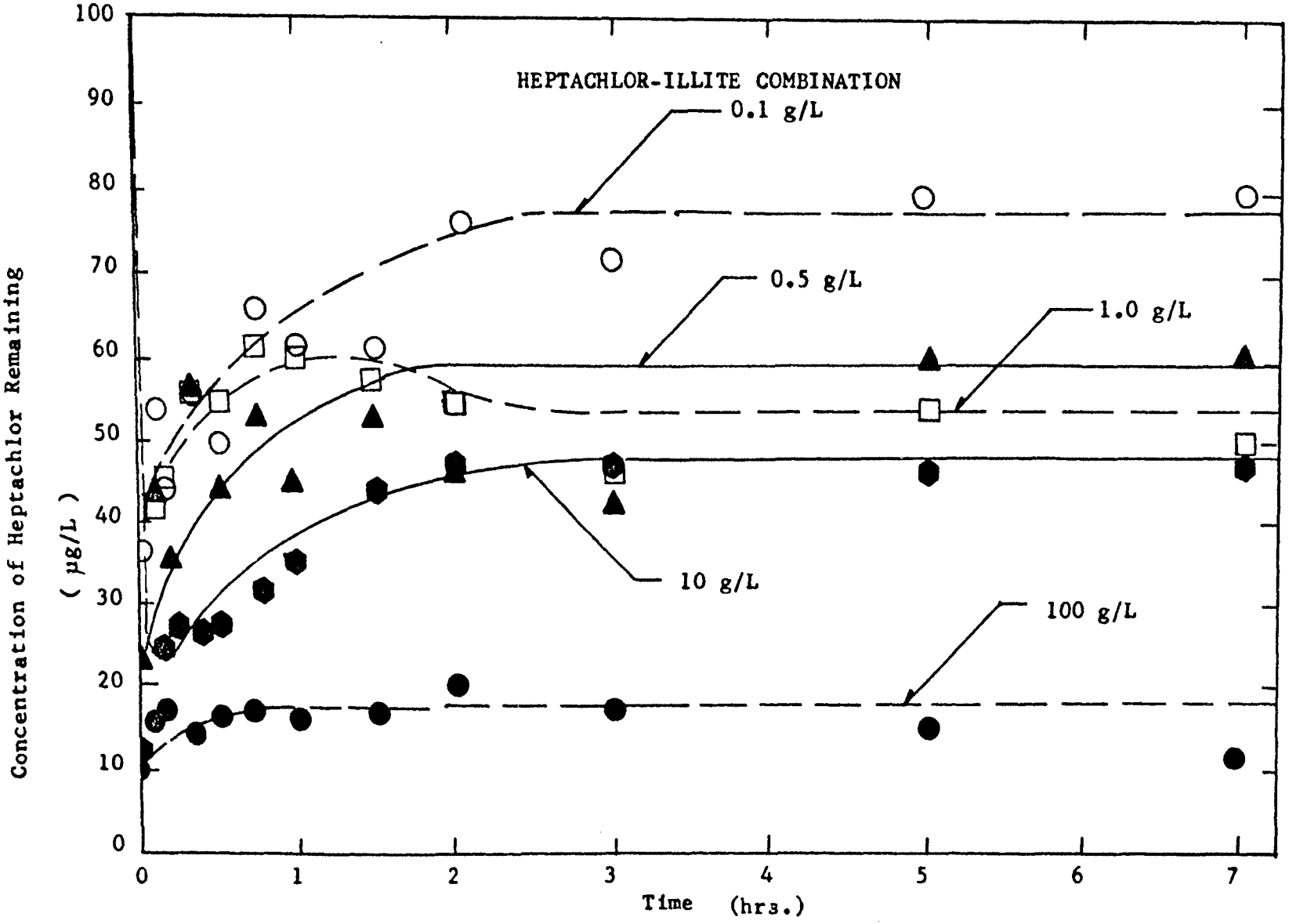

Fig. A3-1. Rate of Adsorption of Heptachlor on Illite

Table A3-2. Rate of Adsorption of Heptachlor on Kaolinite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	10	4.5	15	5.7	22	5.9	39	6.3	48	6.2
5 min.	11	4.5	20	5.2	22	6.0	40	6.2	48	5.8
10 min.	13	4.4	22	5.1	21	5.5	39	5.7	48	5.9
20 min.	16	4.5	20	5.1	27	6.1	43	5.8	47	5.8
30 min.	13	4.5	19	5.1	28	6.1	44	5.8	48	5.8
45 min.	14	4.5	22	5.1	24	5.7	42	5.8	52	5.8
1 hr.	12	4.5	22	5.2	28	5.8	43	5.8	50	5.8
1½ hr.	13	4.5	23	5.3	31	5.7	38	5.8	54	5.8
2 hr.	14	4.5	23	5.2	25	5.6	47	5.7	55	5.7
3 hr.	15	4.5	23	5.2	28	5.6	42	5.7	54	5.7
5 hr.	17	4.5	23	5.2	30	5.7	43	5.8	53	5.8
7 hr.	17	4.5	20	5.2	37	5.6	39	5.7	53	5.6

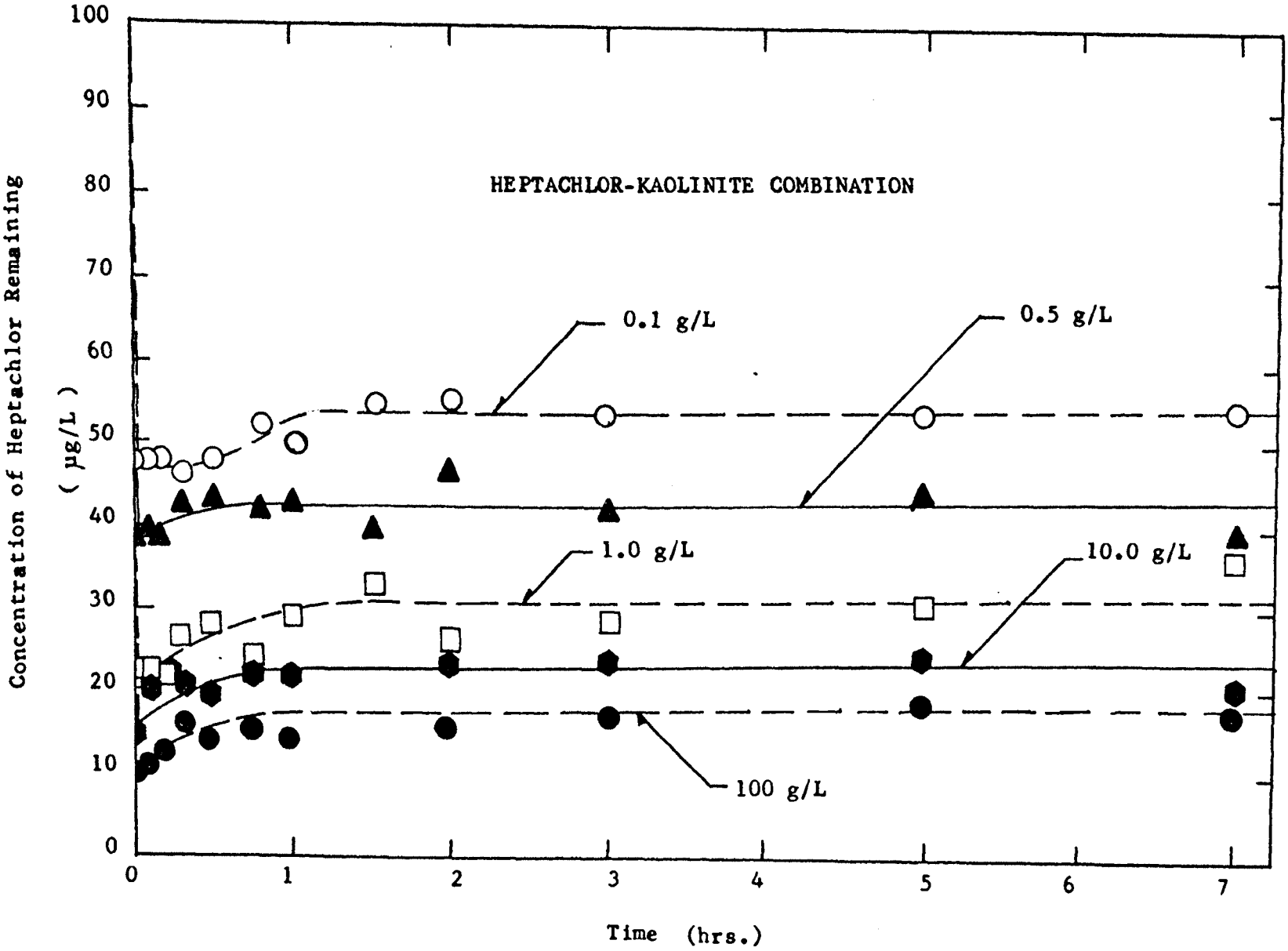

Fig. A3-2. Rate of Adsorption of Heptachlor on Kaolinite

Table A3-3. Rate of Adsorption of Heptachlor on Montmorillonite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	10	4.2	16	4.7	20	5.2	24	5.5	25	6.2
5 min.	9	4.3	16	4.8	29	5.2	34	5.7	31	6.4
10 min.	13	4.4	24	4.9	29	5.2	30	5.7	48	6.1
20 min.	14	4.4	24	4.9	38	5.3	30	5.5	54	6.5
30 min.	16	4.5	25	4.9	38	5.3	36	5.7	56	6.3
45 min.	24	4.4	28	5.0	32	5.3	40	5.8	48	6.2
1 hr.	21	4.6	32	5.1	34	5.3	35	5.4	52	5.9
1½ hr.	17	4.5	30	5.1	30	4.8	42	5.7	52	6.2
2 hr.	20	4.4	28	4.9	29	5.5	42	5.7	44	6.2
3 hr.	17	4.7	25	5.1	26	5.6	42	5.7	52	6.1
5 hr.	16	4.1	22	5.0	29	5.5	42	5.7	56	6.1
7 hr.	16	4.8	24	5.3	30	5.5	44	5.8	58	6.2

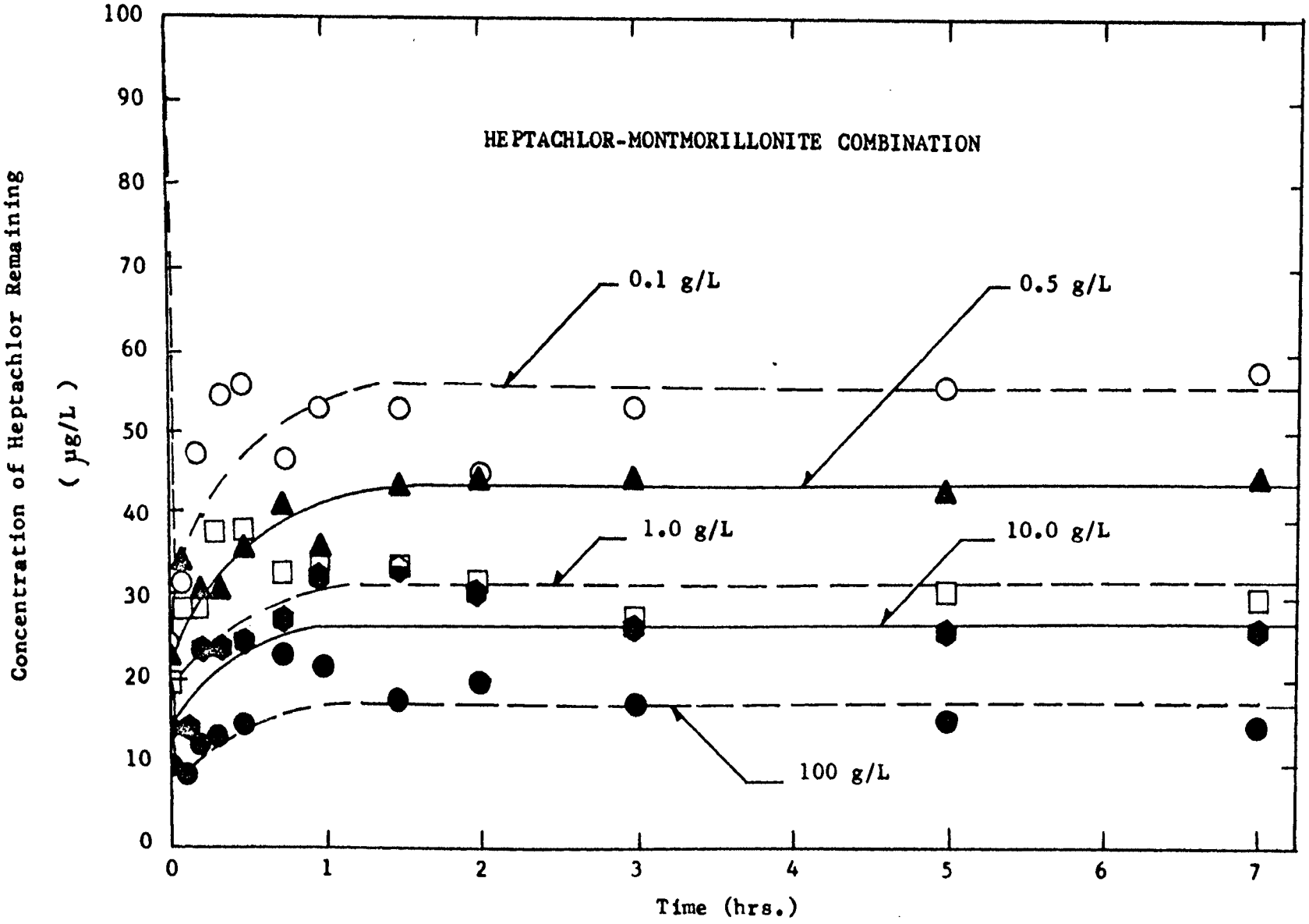

Fig. A3-3. Rate of Adsorption of Heptachlor on Montmorillonite

Table A3-4. Rate of Adsorption of Dieldrin on Illite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	52	8.4	46	8.0	90	6.8	80	6.9	80	6.6
5 min.	52	8.5	72	8.1	95	7.9	90	6.7	80	6.5
10 min.	60	8.6	75	7.8	92	7.0	85	6.9	82	6.6
20 min.	60	8.5	60	7.9	92	7.0	80	7.1	80	6.8
30 min.	60	8.6	56	7.9	92	7.9	82	7.0	92	6.8
45 min.	52	8.6	46	7.8	95	7.1	85	7.1	65	6.9
1 hr.	60	8.4	56	7.8	96	7.1	84	7.1	87	6.9
1½ hr.	60	8.5	58	8.0	90	7.2	87	7.2	86	6.8
2 hr.	50	8.7	72	7.9	70	7.5	80	7.5	87	7.4
3 hr.	42	8.4	65	7.9	85	7.4	87	7.0	90	7.0
5 hr.	48	8.4	70	7.9	75	7.4	82	7.0	82	7.0
7 hr.	44	8.3	68	8.1	82	7.5	80	7.1	86	7.0

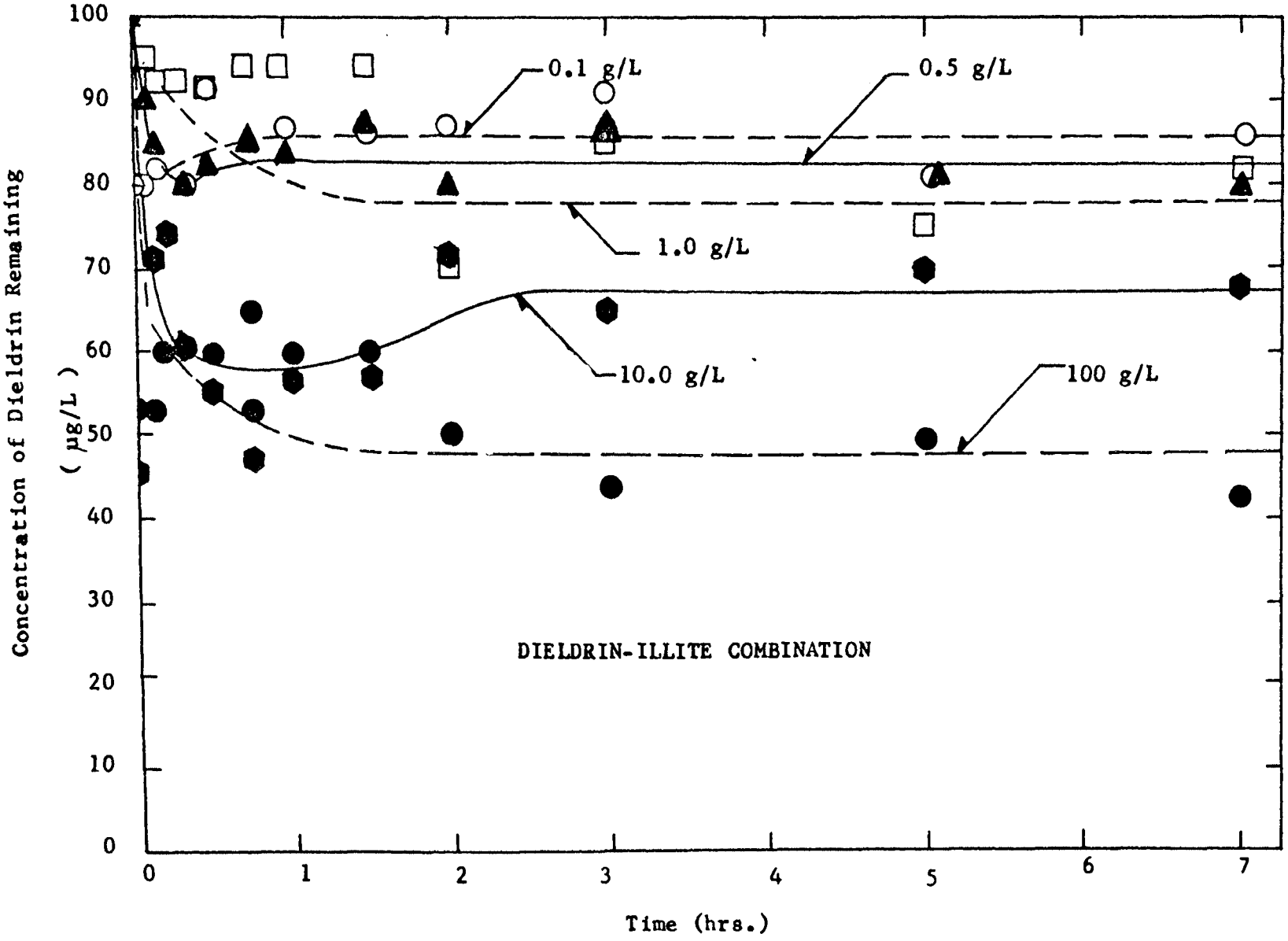

Fig. A3-4. Rate of Adsorption of Dieldrin on Illite

Table A3-5. Rate of Adsorption of Dieldrin on Kaolinite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	34	4.5	40	5.3	45	6.2	52	6.4	55	6.5
5 min.	40	4.5	45	5.3	42	6.2	54	6.4	56	6.6
10 min.	46	4.6	50	5.3	41	6.4	58	-	68	-
20 min.	48	4.6	46	5.4	55	6.3	57	6.6	58	6.8
30 min.	50	4.6	56	5.3	56	6.7	67	6.7	70	6.9
45 min.	-	-	-	-	-	-	-	-	-	-
1 hr.	60	4.6	55	5.4	64	6.6	58	6.7	62	6.8
1½ hr.	50	4.6	62	5.6	46	6.6	64	6.5	56	7.4
2 hr.	62	4.6	65	5.7	60	6.6	65	6.8	62	6.9
3 hr.	66	4.6	76	5.4	66	6.6	67	6.9	62	7.1
5 hr.	70	4.6	70	5.5	74	6.5	74	7.0	74	7.2
7 hr.	62	4.8	75	5.4	68	6.5	75	6.9	75	6.9

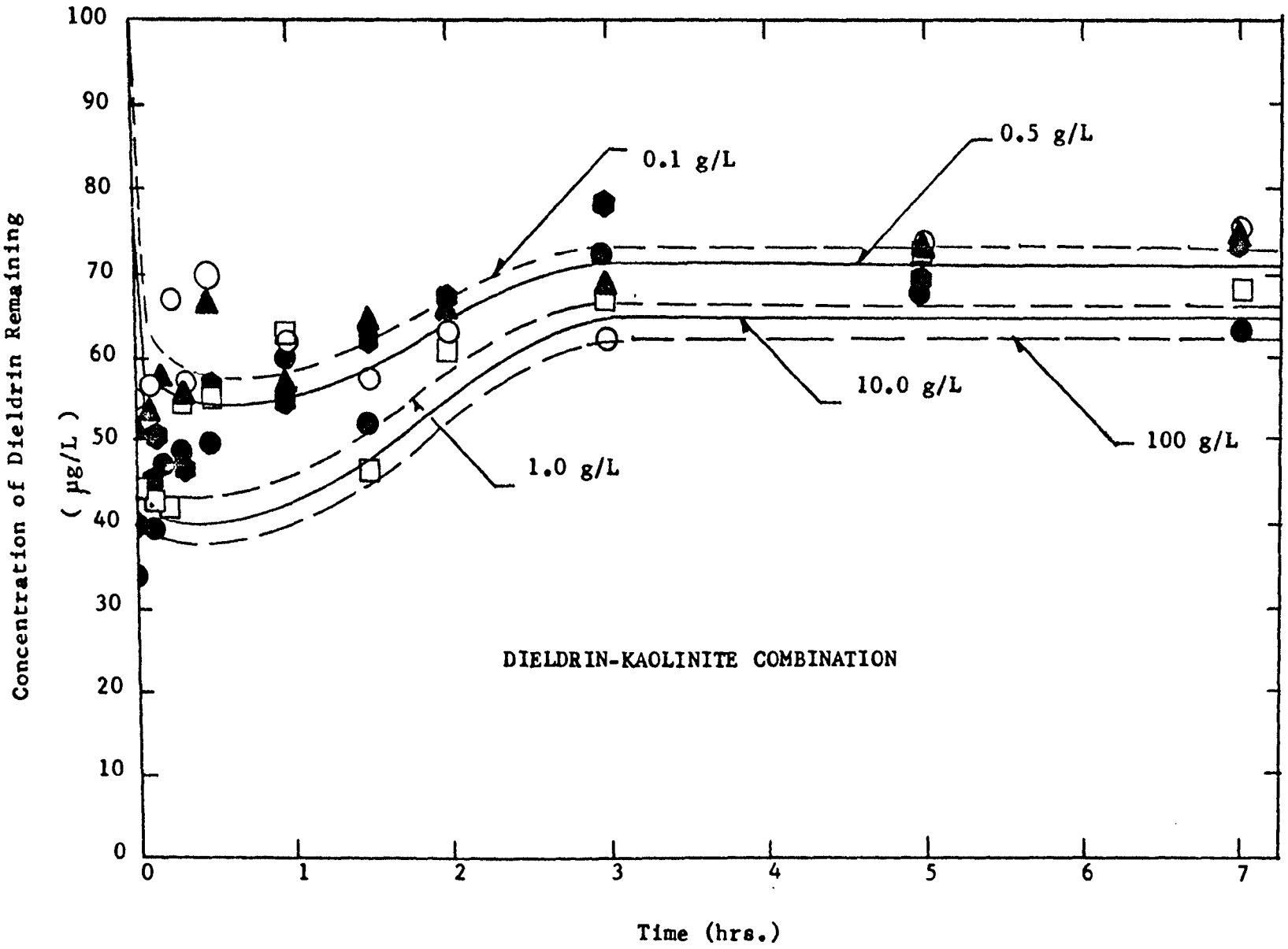

Fig. A3-5. Rate of Adsorption of Dieldrin on Kaolinite

Table A3-6. Rate of Adsorption of Dieldrin on Montmorillonite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	51	4.7	74	4.9	93	5.5	88	5.6	77	5.7
5 min.	44	4.8	82	4.9	90	5.5	89	5.6	81	5.7
10 min.	44	4.8	76	4.9	85	5.4	83	5.6	83	5.7
20 min.	45	4.9	78	4.9	93	5.5	83	5.6	77	5.6
30 min.	47	5.0	71	4.9	89	5.5	88	5.6	73	5.6
45 min.	51	5.0	81	5.0	89	5.7	85	4.5	73	5.4
1 hr.	51	5.0	73	5.3	87	5.5	91	4.7	80	5.6
1½ hr.	55	5.1	77	5.2	82	5.5	72	4.9	77	5.6
2 hr.	48	5.1	71	5.2	68	5.5	85	5.7	70	5.8
3 hr.	46	5.0	61	5.3	85	5.7	75	5.7	74	5.6
5 hr.	39	5.3	48	5.4	82	5.8	76	5.9	72	6.0
7 hr.	46	5.3	61	5.4	78	5.8	78	6.0	81	5.8

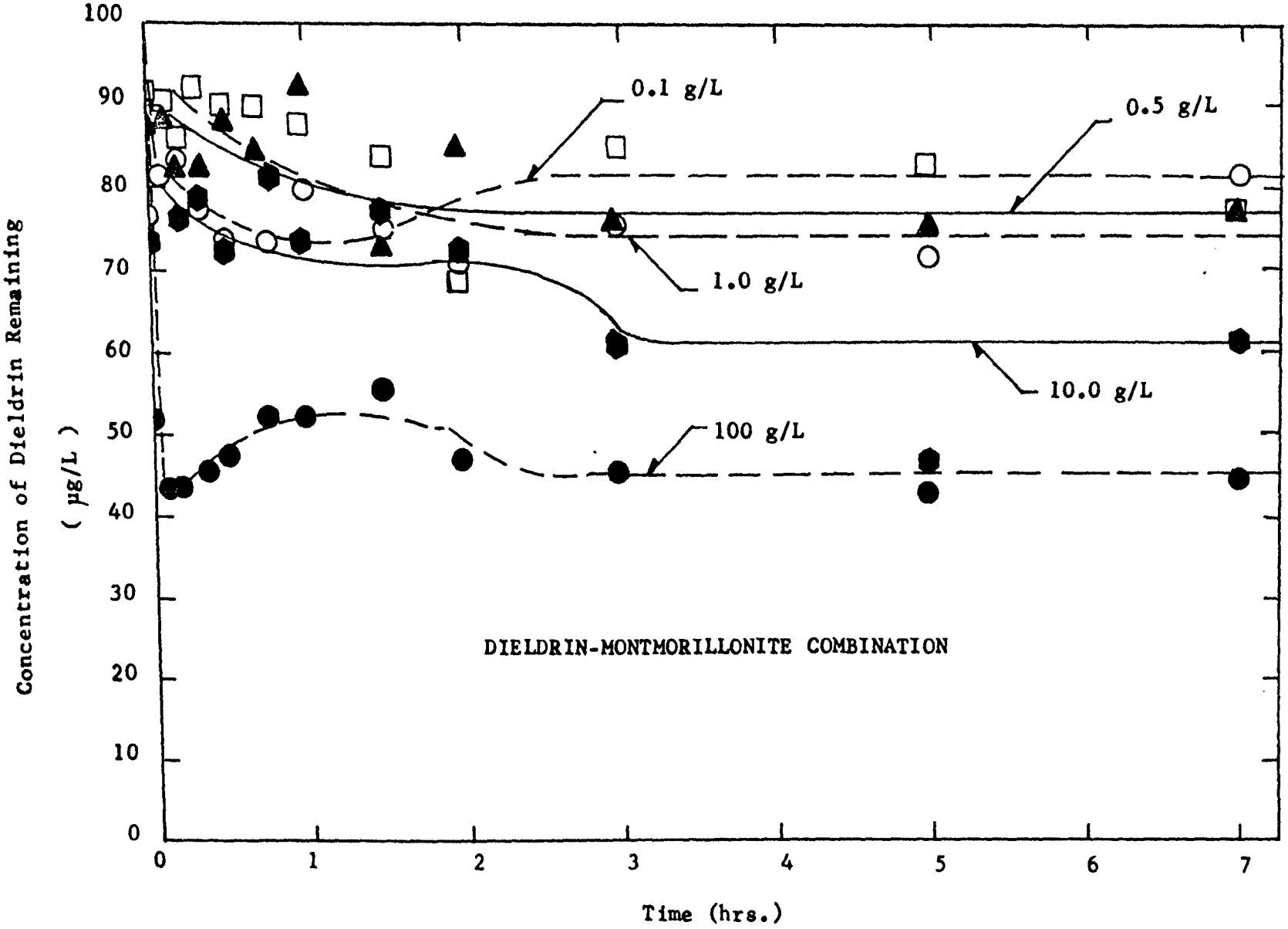

Fig. A3-6. Rate of Adsorption of Dieldrin on Montmorillonite

APPENDIX IV

RESULTS OF THE UPTAKE RATE STUDIES--SECOND EXPERIMENTAL RUN

Presented in this apprendix are the results obtained from the second experimental run of the uptake rate studies (see Chapter V). The data are tabulated in Tables A4-1 through A4-9. Plots for these data have been presented in Chapter V.

Table A4-1. Rate of Adsorption of DDT on Illite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	0	8.3	19	8.2	22	7.7	39	6.7	37	6.5
5 min.	0	8.5	17	8.6	25	7.1	40	6.9	37	6.5
10 min.	0	8.5	8	8.4	17	6.8	15	6.8	18	6.5
20 min.	0	8.6	6	8.6	23	7.0	28	6.7	22	6.4
30 min.	0	8.7	6	8.7	17	7.0	27	6.7	26	6.4
45 min.	0	8.4	10	8.7	17	7.0	27	6.7	20	6.5
1 hr.	0	8.6	10	8.5	15	7.0	18	6.7	23	6.4
1½ hr.	0	8.6	9	8.3	13	6.7	20	6.6	26	6.5
2 hr.	0	8.6	7	8.0	14	6.7	17	6.6	24	6.4
3 hr.	0	8.4	3	7.7	18	6.6	17	6.5	26	6.5
5 hr.	0	8.4	8	7.9	13	6.7	21	6.6	23	6.4
7 hr.	0	8.5	10	7.6	15	6.6	18	6.6	25	6.5

Table A4-2. Rate of Adsorption of DDT on Kaolinite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	0	3.9	15	4.8	41	5.4	53	5.9	67	6.0
5 min.	0	4.0	17	4.8	41	5.4	46	5.6	61	5.6
10 min.	0	4.0	16	4.8	24	5.4	45	5.5	48	5.6
20 min.	0	4.0	6	4.8	17	5.4	31	5.6	41	6.3
30 min.	0	4.2	13	4.9	23	5.4	19	5.8	38	5.6
45 min.	0	4.3	7	4.9	22	5.4	14	5.5	32	5.6
1 hr.	0	4.2	7	4.9	15	5.5	12	5.6	29	5.6
1½ hr.	0	4.3	7	4.9	8	5.3	9	5.5	29	5.5
2 hr.	0	4.3	6	4.9	7	5.4	7	5.5	25	5.5
3 hr.	0	4.3	5	4.9	10	5.4	11	5.5	25	5.4
5 hr.	0	4.3	5	5.1	11	5.5	9	5.6	24	5.7
7 hr.	0	4.4	7	5.0	11	5.4	12	5.4	27	5.6

Table A4-3. Rate of Adsorption of DDT on Montmorillonite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	0	4.6	23	5.2	52	5.3	68	5.7	60	5.8
5 min.	0	4.6	19	5.2	40	5.6	60	5.7	68	5.8
10 min.	0	4.6	14	5.2	48	5.5	57	5.8	60	5.8
20 min.	0	4.7	12	5.2	46	5.6	60	5.8	60	6.2
30 min.	0	4.6	19	5.2	46	5.6	52	5.8	40	6.2
45 min.	0	4.6	13	5.2	44	5.9	39	5.7	40	5.8
1 hr.	0	4.6	12	5.2	34	5.5	22	5.6	40	5.7
1½ hr.	0	4.4	7	5.2	32	5.5	26	5.8	26	5.7
2 hr.	0	4.3	14	5.2	30	5.6	32	5.5	26	5.7
3 hr.	0	4.6	12	5.2	36	5.5	30	5.6	26	5.7
5 hr.	0	4.7	10	5.4	20	5.6	30	6.1	26	6.2
7 hr.	0	4.3	12	5.4	24	5.6	22	5.7	27	5.7

Table A4-4. Rate of Adsorption of Heptachlor on Illite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	20	8.7	50	8.3	44	7.3	65	7.5	74	7.2
5 min.	12	8.8	50	8.4	49	7.5	53	7.6	64	7.2
10 min.	11	8.8	47	8.4	48	7.5	51	7.5	65	7.3
20 min.	10	8.9	50	8.4	33	7.5	49	7.4	67	7.3
30 min.	10	8.9	44	8.6	34	7.6	53	7.3	75	7.2
45 min.	11	8.9	45	8.7	37	7.2	46	7.2	69	6.8
1 hr.	12	8.9	45	8.8	39	7.4	43	7.3	70	7.2
1½ hr.	8	8.9	39	8.9	33	7.4	44	7.1	63	7.1
2 hr.	9	8.9	26	8.7	30	7.5	48	7.3	69	7.2
3 hr.	7	8.8	27	8.6	33	7.2	48	7.0	64	6.9
5 hr.	8	8.8	22	8.8	35	7.1	50	7.0	67	7.1
7 hr.	9	8.8	23	8.9	34	7.7	47	7.7	68	7.5

Table A4-5. Rate of Adsorption of Heptachlor on Kaolinite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	8	5.9	31	6.1	34	6.3	50	6.3	61	6.6
5 min.	11	6.0	30	6.3	32	6.4	43	6.8	49	6.5
10 min.	10	6.0	27	6.3	46	6.4	37	6.4	41	6.4
20 min.	9	6.0	27	6.4	48	6.2	46	6.2	53	6.3
30 min.	10	6.1	24	6.3	45	6.4	50	6.3	57	6.3
45 min.	9	6.2	22	6.4	33	5.9	34	6.3	58	6.4
1 hr.	10	6.2	28	6.3	39	6.0	32	6.3	49	6.4
1½ hr.	9	6.0	27	6.4	33	6.1	45	6.2	54	6.4
2 hr.	8	6.3	28	6.6	41	6.2	43	6.3	56	6.4
3 hr.	13	6.1	24	6.3	39	6.4	44	6.6	59	6.5
5 hr.	11	6.4	25	6.4	41	5.8	41	6.0	60	6.6
7 hr.	12	6.4	26	6.5	39	6.0	45	6.2	61	6.8

Table A4-6. Rate of Adsorption of Heptachlor on Montmorillonite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	17	4.8	57	5.5	57	5.7	65	6.0	80	6.0
5 min.	13	4.9	53	5.5	56	5.7	66	5.9	70	6.0
10 min.	5	4.9	47	5.6	56	5.7	74	5.9	90	6.0
20 min.	8	4.7	39	4.7	54	5.8	64	5.9	85	6.0
30 min.	8	5.0	35	5.3	60	5.8	57	6.0	82	6.0
45 min.	7	5.0	43	5.5	60	5.8	56	5.7	62	6.0
1 hr.	9	5.0	22	5.6	49	5.9	49	6.1	39	5.8
1½ hr.	6	5.0	33	5.4	37	5.8	73	5.9	40	6.1
2 hr.	4	5.1	16	5.6	22	5.9	61	5.8	50	5.7
3 hr.	4	5.1	23	5.6	52	5.8	45	5.8	55	5.7
5 hr.	5	5.2	20	5.4	41	5.8	46	5.8	50	5.9
7 hr.	6	5.1	40	5.7	53	5.8	56	5.6	61	5.9

Table A4-7. Rate of Adsorption of Dieldrin on Illite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	49	8.7	73	8.4	80	7.6	87	7.4	75	7.6
5 min.	43	8.7	77	8.4	81	7.3	74	7.4	76	7.4
10 min.	39	8.8	75	8.4	81	7.4	76	7.4	78	6.9
20 min.	30	8.8	68	8.4	85	7.3	77	7.4	77	7.4
30 min.	26	8.8	67	8.5	83	7.5	73	7.5	77	7.5
45 min.	27	8.8	64	8.7	86	7.5	75	7.4	83	7.3
1 hr.	25	8.9	65	8.7	77	7.4	80	7.0	82	7.2
1½ hr.	31	8.9	57	8.6	77	7.2	79	7.0	84	7.0
2 hr.	33	8.9	58	8.6	75	7.4	78	7.2	85	7.0
3 hr.	28	8.8	34	7.1	76	7.5	82	7.1	83	7.0
5 hr.	34	8.7	45	8.3	76	7.0	84	6.8	86	6.9
7 hr.	36	8.6	56	8.2	76	7.0	82	6.9	86	7.1

Table A4-8. Rate of Adsorption of Dieldrin on Kaolinite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	65	4.0	77	5.2	79	6.3	86	6.4	88	6.7
5 min.	58	4.1	76	4.7	82	5.7	86	6.0	82	6.1
10 min.	61	4.1	74	4.9	77	6.7	86	6.0	82	6.1
20 min.	70	4.1	74	4.8	75	5.7	78	6.0	83	6.0
30 min.	68	4.2	68	4.9	75	5.8	77	6.0	86	6.2
45 min.	64	4.2	68	4.9	71	5.8	82	6.0	84	6.0
1 hr.	66	4.2	77	4.9	76	5.7	77	6.0	89	6.0
1½ hr.	64	4.4	77	4.9	78	5.7	86	5.9	81	6.0
2 hr.	62	4.4	71	4.9	78	5.7	84	5.8	88	5.9
3 hr.	65	4.4	71	5.0	82	5.6	87	5.8	83	6.0
5 hr.	64	4.4	70	5.0	80	5.5	85	5.9	86	6.0
7 hr.	61	4.4	72	5.2	82	5.2	86	5.9	88	6.2

Table A4-9. Rate of Adsorption of Dieldrin on Montmorillonite

Time of Reaction	Pesticide Remaining and pH in the Suspension Having a Clay Concentration of									
	100 mg/l		10 mg/l		1 mg/l		0.5 mg/l		0.1 mg/l	
	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH	Pesticide Residue (ppb)	pH
2 min.	28	4.7	50	5.1	63	5.7	74	5.8	86	6.0
5 min.	28	4.6	44	5.1	65	5.8	67	5.8	86	5.9
10 min.	31	4.7	44	5.3	60	5.8	-	5.8	78	5.8
20 min.	28	4.7	52	5.3	65	6.0	72	6.0	82	6.1
30 min.	40	5.3	52	5.7	72	6.0	72	6.2	-	6.4
45 min.	36	5.0	50	5.7	76	6.2	72	6.3	86	6.2
1 hr.	39	5.0	56	5.9	76	6.2	75	6.3	90	6.4
1½ hr.	39	4.6	63	5.2	75	5.9	80	6.0	88	5.8
2 hr.	39	4.5	56	5.2	75	5.7	76	5.8	90	5.9
3 hr.	39	4.5	52	5.1	75	5.8	80	5.9	88	6.2
5 hr.	39	4.5	64	5.2	76	5.5	84	5.9	90	6.2
7 hr.	39	4.6	63	5.3	76	5.8	86	6.1	90	6.3

VITA

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Following graduation, he joined the Chinese Army for his one year ROTC program. Upon his discharge from the military service, he was employed by the Chinese Army Institute of Technology and 6217th Civil Engineering Squadron of the U.S. Air Force. He came to the United States in January, 1968 to pursue his graduate study at the University of Missouri-Rolla.

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